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A Dendrochemical Analysis of Lead, Aluminum, and Calcium in Southern Appalachian American Beech.

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Dendrochemical Analysis of Lead, Aluminum, and Calcium in Southern Appalachian American Beech

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ABSTRACT

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The health of the northern hardwood forest in the Southern Appalachian Mountains of Tennessee, North Carolina, and Virginia has recently gained attention from the media and environmental stakeholders. This project was designed to examine concentrations of metals, including lead, aluminum, and calcium in growth rings of an important northern hardwood species, American beech *(Fagus grandifolia* Ehrh.*)* at Mount Rogers and Whitetop Mountain, Virginia. Dominant and codominant trees were sampled from 16 research plots located at two different elevations. Samples were crossdated, divided into sections of 10-year periods, and analyzed using atomic absorption spectroscopy. Concentrations of metals were negatively correlated with ring width. Elevation and aspect were significantly associated with the concentration of the cations analyzed. Both lead and calcium concentrations increased during the 1860s and again during the mid-1900s. This increase in lead and calcium may suggest the mobilization of these elements in soil.

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CHAPTER 1

INTRODUCTION

The present is the key to the past.

James Hutton 1785

Factors influencing ecosystem health are often not evident. Changes in an environment are usually the result of an event or a series of events occurring over time. To conduct research on such phenomena, scientists will either spend many years observing response to change or will sample for a short time period, taking a particular "snapshot of time" to examine environmental alterations. Seasonal variation may affect the fate and impact of stressors requiring seasonal data collection to allow adequate evaluation of impact.

Forest ecosystem health may be influenced by events that occur over a long period of time. Not all stages of disturbance are apparent at the time of monitoring; therefore, it would be beneficial to use methods that allow the detection of temporal changes. Examinations of tree-rings supply data relevant to the entire lifespan of a tree that provides information about growth and associated seasonal effects. Monitoring of forest health involves looking at changes in the ecosystem that may be caused by stressors such as pollution or disease. Certain environmental influences encourage the mobilization of chemicals that may be taken up by the tree instead of, and in addition to, beneficial nutrients.

While spruce-fir decline in southern Appalachian forests has received much focus in the past twenty years (Nicholas et al. 1999), published data regarding northern hardwood forest health in the southern Appalachian Mountains is scarce. However, health of the northern hardwood forest in the southern Appalachian Mountains of Tennessee, Virginia, and North Carolina has recently received media attention. Several environmental stakeholder groups have suggested that forest condition has deteriorated in stands above 1,370 meters in elevation and link this purported decline to high levels of air pollution (Nicholas et al. 2000). High elevations in the southern Appalachian Mountains are exposed to higher levels of pollutant loading than

lower elevations due to increased precipitation and frequent immersion in clouds (Mohnen 1992).

This project was developed to determine chemical concentrations throughout the lifespan of a northern hardwood species found in the southern Appalachians. Comparing the concentrations of elements in tree-rings with the amount of growth during a particular time period may provide an explanation of growth patterns attributed to abiotic and biotic stressors. American beech (*Fagus grandifolia*, Ehrh.*),* a common northern hardwood species, was chosen because of its good qualities for dendrochemical analysis, which include good heartwood permeability, low heartwood moisture content, mixed attributes in the number of rings, species pervasiveness, longevity, wide geographic distribution, and foliage type. These criteria were based on habitat-, xylem-, and chemical factors (Cutter and Guyette 1993). Based on results obtained during this study it appears that dendrochemical analysis of American beech can be used as an indicator of forest health history.

Objectives

This study examined the concentrations of calcium, lead, and aluminum in the annual growth rings of American beech on Mount Rogers and Whitetop Mountain, in southwest Virginia to determine if there is a correlation between growth and cation concentrations. In addition, aluminum to calcium concentration ratios were tested for association with growth. The objectives of this study were to 1) age and crossdate tree-ring increment cores of American beech sampled from Mount Rogers and Whitetop Mountain, Virginia to determine the annual growth rate; 2) analyze association between growth and cation concentration changes through time; 3) identify the concentration of lead, aluminum, and calcium, by decade, in annual growth rings of American beech; and 4) compare the concentrations of aluminum, calcium, and lead in tree rings at two different elevations (1,371m and 1,524m) on Mount Rogers and Whitetop Mountain, Virginia.

CHAPTER 2
REVIEW OF LITERATURE

The Southern Appalachian Northern Hardwood Forest

The southern Appalachian northern hardwood forest occupies a small area of the hardwood forest contained in the southeastern United States, comprising a total of 3.42 X 10^7 ha of hardwood forestland. The southern Appalachian northern hardwood forest is located in the southwestern tip of Virginia, southeastern Kentucky, northeastern Tennessee, western North Carolina, and northern Georgia (NAPAP 1991). Species of northern hardwoods occupying the southern Appalachian region include: sugar maple (*Acer saccharum* Marsh.), white oak (*Quercus alba* L.), black oak (*Q. velutina* Lam.), and northern red oak (*Q. rubra* L.), American beech, and yellow birch (*Betula alleghaniensis* Britt.). These species are found in moist coves and on slopes between 1,065 and 1,675 m in elevation (Smith 1980). American beech found at higher elevations also exist with red spruce (*Picea rubens* Sarg.), Fraser fir (*Abies fraser* (Pursh) Poir.), yellow birch, and red maple (*Acer rubrum* L.) (Smith and Linnartz 1980). The maple-beech-birch forest classified within the hardwood forest types occupies a small area of 96,000 ha within the total hardwood forests found in the southeastern United States (NAPAP 1991). American beech extends from Nova Scotia in Canada down through northern Michigan, Wisconsin, southern Illinois then into Arkansas, Oklahoma, eastern Texas, and east to northern Florida. The west to east range of this area extends from the Mississippi River to the eastern seaboard (Millers et al. 1988).

The concern over the mortality and decline of northern hardwood trees in the eastern United States in the 1980s prompted the creation of the Eastern Hardwoods Research Cooperative (EHRC) in 1987, which was part of the Forest Response Program (FRP), a research effort created within the National Acidic Precipitation Assessment Program (NAPAP). The FRP operated, as part of the Terrestrial Effects Task Group within NAPAP and addressed the environmental policy questions: Is there significant forest damage in North America; and if so, could it be attributed to acidic deposition alone? Is there a causal relationship between air pollutants and forest damage? What is the relationship between air pollutants and the damage; and is it stand or regionally based? (NAPAP 1991) The objective of the Eastern Hardwood

Research Cooperative was to identify spatial relationships among atmospheric deposition, pollutant exposure and forest health. Primarily, the objectives included providing case studies of major eastern hardwood decline through documentation of species type and distribution, climate, and deposition patterns while documenting the location, history, and severity of decline. Attempts were made to determine if the frequency of decline differed from that of past occurrences, and if there were reasons for disturbance such as insect infiltration or the presence of damaging agents included in atmospheric deposition (Millers et al. 1988). Research conducted for the EHRC focused on eastern areas of the United States including Pennsylvania, Arkansas, Ohio, and northern Midwest states such as Minnesota and Michigan (NAPAP 1991).

Millers et al. (1988) published a concise history of the hardwood decline in the Eastern United States. They focused on the literature of forest declines, primarily from major books and reviews. American beech mortality and decline was linked to drought and severe winters in New York and West Virginia beginning in the 1950s. Mortality from the oyster shell scale insect infestation caused the loss of more than 30% of American beech in Pennsylvania and 10 to 15% in Maine. Millers et al. did not find significant evidence to suggest a link between high levels of atmospheric pollution and tree mortality.

The effects of anomalous characteristics possibly related to atmospheric deposition on forest health were assessed along a wet sulfate/ pH deposition gradient in north-central Pennsylvania (Nash et al. 1992). Tree crown evaluations were used to determine the health of 13 analogous hardwood stands and it was determined that there was no relationship between health and deposition patterns.

Tree-ring samples of American beech, yellow birch, northern red oak, eastern hemlock (*Tsuga Canadensis* (L.) Carr), and white ash (*Fraxinus americana* L.) were collected to investigate growth decline. Growth reduction occurred in the hardwood species; however, this coincided with documented cases of insect defoliation and drought. Adverse effects caused by air pollution were ruled out because of the absence of unusual or reduced growth (NAPAP 1991).

The majority of research under the EHRC was conducted in the northeastern and Midwest states during the 1980s. Northern hardwood decline in the southern Appalachian Mountains has recently gained attention from the media. However, data from the USDA Forest

Service's Forest Inventory Analysis databases indicate the total area affected by mortality and decline in this area is between 500-1,000 acres, or 0.5-1% of the northern hardwood forest found within this region (USFS 1997).

Principles of Dendrochronology

Dendrochronology is a tool used to measure decades or centuries of environmental influence on trees. Grissino-Mayer (1999) defines dendrochronology in a personal web page as, "a science that uses tree rings dated to their exact year of formation to analyze temporal and spatial patterns of processes in the physical and cultural sciences." One advantage of using dendrochronology, as an indicator of ecosystem health is the amount of time that is conserved. Data that would normally take decades to collect is preserved within the increment core, making these otherwise unavailable chemical data available to researchers. Evaluation of these seasonal impacts is made possible by the addition of a layer of growth during each growing season, resulting in an increase in height and breadth. The vascular cambium is responsible for increasing the tree's diameter by producing tissue, which adds a new layer of xylem producing a ring (Stokes and Smiley 1968).

Growth rings are produced in response to environmental fluctuations. The width of a tree-ring is influenced by growth conditions, with larger widths signifying more favorable conditions (Schweingruber 1993). The annual rings will reflect the environmental conditions during two phases of growth based on the appearance of earlywood and latewood. Earlywood may be described as an annual ring formed at the beginning of each growing season, which is wide and light in coloration. Latewood is formed at the end of a growing season producing a narrower, darker ring (Stokes and Smiley 1968). Each year is, therefore, made up of both an earlywood and a latewood ring. Environmental influences that may determine the appearance of ring formation include the occurrence of drought conditions, soil moisture, chemistry and texture, temperature, and exposure to pollution (Stokes and Smiley 1968).

Tree-Ring Interpretation

The determination of tree age requires that a cross-section of the bole be taken to measure rings from the center of the tree, known as the pith, to the bark. One way to collect the cross section data is to use an increment borer to remove an inner portion of the tree at or near breast height (1.37 meters above the ground). Removing the core at breast height is done to prevent coring where the ring patterns are likely to be distorted by compression of wood, underneath branches and the uphill or downhill sides of the trunk (Zedaker and Nicholas 1990). After removal the number of earlywood and latewood sections in the tree core are counted from the center of the core sample to the bark to determine how many years the tree has produced rings. The number of tree-rings counted determines the age of the tree the year it was cored.

Factors Affecting Ring Development

Because of species and site differentiation, each tree will exhibit growth characteristics distinct from other trees. Growth rates are affected by the most limiting condition in a particular area (Fritts 1976). Years of drought or harsh conditions may result in a ring becoming so narrow that it may not appear at each point in the stem growth, consequently not seeming to appear at all (Stokes and Smiley 1968). This is known as a missing ring. Missing rings, if undetected, may cause unintentional discrepancy in data; therefore, it is essential to make every attempt to account for inconsistencies within ring patterns. One method used to reduce this error is to crossdate. Tree species growing within a specific region will produce similar ring patterns as a result of analogous growing conditions. While total growth may differ between species, patterns on each ring will match those of another tree growing in the same microclimate, providing that the time periods are the same (Stokes and Smiley 1968). Crossdating a series of rings from several trees growing within the same microclimate allows for the identification of the exact year in which the tree ring was formed (Fritts 1976).

Another complication that may arise and confound the accurate age determination is the presence of double rings, also known as false rings. Double rings often occur in annual tree growth when the occurrence of a dark latewood band appears in the early wood growth (Stokes and Smiley 1968). This phenomenon can result in the appearance of two separate years. Sudden climatic changes are thought to contribute to this anomaly (Fritts 1976). To detect such

occurrences, one must note the separation of latewood rings into earlywood, which are sharp contrasting differences, unlike the appearance of false rings, which are a gradual blend into each distinct ring (Stokes and Smiley 1968).

Principles of Dendrochemistry

In addition to revealing growth trends, the annual rings of a tree may also act as an indicator of pollution events, serving as a chronological guide to past chemical exposures (DeWalle et al. 1995). Dendrochemistry is a tool used for the detection of chemicals found within the growth rings of trees (DeWalle et al. 1995). The composition of each annual ring should reflect the chemical constituents present in the environment during ring growth due to the manner in which elements are stored within cells of the tissue.

Absorption of chemicals into the growth rings of trees may occur through several pathways. Root uptake from the soil serves as the main means of diffusion; however, uptake through foliage and bark may also occur (Watmough 1997). The route of ion incorporation varies between tree species and is also influenced by the soil chemistry, hydrology, and nutrient availability (Vimmerstedt and McClenahen 1995). For example, a site that contains low pH soil is more likely to support increased cation uptake because the ions are more soluble in solution, hence more readily available for uptake by the roots.

Storage of Elements

As the tree ages, cells act in different roles to provide structure and nutrients. Storage cells, known as rays, are found in two different areas in the wood: sapwood and heartwood. The sapwood, which is the newly formed wood, is the living, physiologically active area found just within the bark. Heartwood is the older nonfunctioning cells found in the area between the sapwood and the pith of the tree (Cutter and Guyette 1993). Each growing season a tree adds an additional layer of growth. This occurs by a process in which the sapwood ceases to perform and turns into heartwood, thus the addition of annual rings. During this conversion elements that are present in the sapwood as a result of root uptake will become permanently stored in heartwood (Yanosky and Vroblesky 1995).

Factors Affecting Dendrochemistry

Ion concentrations can shift from the year in which they were originally formed into a different year of the growth ring (Watmough 1997). This radial translocation is caused by unequal vertical and lateral transportation rates within a tree, in which vertical transportation of nutrients usually exceeds that of lateral movement. In instances of considerable lateral translocation, the ion concentration within that growing season will shift outward in the sapwood causing a spread that may interfere with the historical record of the ions within the tree-rings (Cutter and Guyette 1993). This occurrence can be attributed to the differences in mobility between certain ions; therefore, selection of ions to be detected should be considered before analysis (Watmough 1997). Detection of aluminum concentration within growth rings is considered by dendrochemists to be a valid biomarker because it is not as often subjected to translocation (Watmough 1997). Translocation and the use of tree rings for lead detection is a satisfactory method for dendrochemical analysis (Symeonides 1979). However, the physiologically process by which trees translocate ions is still not entirely understood.

Role of Acidic Deposition

The formation of wood in trees is affected by the concentration of nutrients a tree is able to absorb. Calcium, magnesium, sodium, and potassium (known as base cations) are essential nutrients that the tree must absorb through the soil (Lawrence and Huntington 1999). Nutrient mobility into trees may be hindered when conditions in the environment modify the soil. Acidic deposition caused by sulfuric and nitric acid in cloudwater, rain, or snow may lower the pH of the soil. This allows elements that are normally sequestered to become available to compete with nutrients at ion exchange sites (Nicholas et al. 1999). Base cations are generally deficient in areas of low pH compared to a smaller percentage of deficiencies found in higher pH soils (Momoshima and Bondietti 1990). Cloudwater acid deposition is prominent in high elevations where trees are subjected to frequent mist and fog conditions. High elevation forest ecosystems contain a higher frequency of growth anomalies in trees (Bondietti et al. 1990).

Acids and other pollutants may also be deposited directly on the forest canopy and soils where there are gaps in the canopy (Tomlinson 1983). Excess hydrogen ions associated with the rising acidity of the soil increase the solubility of aluminum and lead (Tomlinson 1983). High

levels of acidic deposition may also leach base cations from the soil by hydrogen ion displacement, keeping base cations dissolved in the soil water which eventually may be washed into streams (Lawrence and Huntington 1999). Leaching of base cations from soil is thought to be greater at high elevations (Yanai et al. 1999).

If base cations have to compete with elements, they may become displaced, causing the element which has a stronger affinity to become easily attached to the soil and taken up by the root of the tree (Tomlison 1983). The uptake of aluminum and lead can damage root systems, resulting in growth reduction, which may be reflected as a narrow annual growth ring.

Thompson (1981) sampled tree-ring chronologies from singleleaf pinyon pine (*Pinus monophylla* Torr. and Frem.*)* to detect the effect of air pollution emitted during copper smelting. Ring widths from tree samples taken at a site upslope from a copper smelter in McGill, Nevada, were more compressed compared to ring samples obtained from control sites 15-80 km away. The compacted rings in sites affected by the effluent plume were noted in the years between 1910 and 1930, corresponding to a time of increased copper mining. Thompson noted an average increase in ring width as copper production began to slow in 1930-1935.

Robitaille (1981) showed that lead, copper, and zinc concentrations in balsam fir (*Abies balsamea* (L.) Mill.) trees in eastern Canada increased over time. The increase in metals coincided with an increase in $S0_2$-containing acid precipitation resulting in reduced tree growth.

Presence of Aluminum in Tree-Rings

High concentrations of aluminum occur naturally in the soil; however, most of the aluminum is not bioavailable because it is bound to clay portions of the soil. If the soil pH decreases, the aluminum will become more soluble and can bind at ion exchange sites of water molecules in the soil because of the +3 charge (Lawrence and Huntington 1999). Hydrogen ions and aluminum ions in soil solution can displace calcium from root adsorption sites, at a pH 5.0 (Tomlinson 1983). Aluminum in acidic soil may go into solution by the following process (Tomlinson 1983):

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$

Aluminum in this form may then be able to compete with cations needed by the tree. Symptoms of aluminum toxicity in trees include a reduction in root growth, thickening of roots, reduced

root elongation, decreases in fine root branching, decreases in leaf production, and water uptake (Cronan et al. 1989). Aluminum toxicity on root development varies. Toxic concentrations have been noted as low as 0.4 μM and nontoxic concentrations as high as 134 μM. (Adams et al. 1999)

Aluminum concentrations found in the xylem of red spruce downwind from a coal-burning power generator in New Brunswick, Canada, increased in newly formed wood from 0.5 ppm in 1930 to 1 ppm in 1980 (Arp and Manasc 1987). Arp and Manasc suggested these trends are related to SO_2 emissions resulting in acidic deposition. They found a gain of water-soluble and bicarbonate extractable $S0_4$ and decreased magnesium exchangeability in soil close to the power plant. Tree-ring measurements showed that growth increased until 1960 and then declined.

Zayed and Loranger (1992) sampled red spruce tree cores from 31 sites in an industrialized region of Quebec, Canada, to analyze changes in metal concentration. Concentrations of aluminum increased in wood older than 5 years. Trees with higher metal concentrations were growing in towns where metal refineries were present.

Levy et al. (1996) conducted a tree-ring analysis on the heartwood of pendunculate oaks (*Quercus. robur* L. and *Q. petraea* (Matt) Liebl.*)* to investigate the relationship between temporal cation trends and soil properties. Aluminum gradually increased from 11mg Al^{+3} kg^{-1} in 1949 to 35 mg Al^{+3} kg^{-1} in 1974. They suggested that acidification of the soil may have been caused by the close proximity of steel manufacturing and that this was responsible for the increased uptake of aluminum into the trees.

Joslin and Wolfe (1992) studied soil solution chemistry and root distribution in red spruce exposed to cloudwater deposition on Whitetop Mountain, Virginia. Aluminum concentrations of 320μmol L^{-1} exceeded the 250μmol L^{-1} toxicity threshold for red spruce root growth in high-cloud established plots (1,676 meters). The authors noted a relationship between low root biomass in plots located at areas of high-cloud elevations and high Al concentrations.

Baes and McLaughlin (1984) showed increased zinc, aluminum, copper, iron, and chromium concentrations in the radial patterns of shortleaf pine (*Pinus echinata* Mill.) tree-rings in eastern Tennessee. These increases were noted during the two to three decades previous to

their study; a result, the authors suggested, of recent increases in the deposition of these elements.

Aluminum: Calcium Nutrient Availability

Calcium, an essential nutrient for the health and growth of a tree, is used for the formation of wood (Lawrence and Huntington 1999). If cations in the soil are solubilized, competition for uptake between calcium and other cations may occur. Aluminum ions have a +3 charge and calcium ions have a +2 charge. Because of this difference, aluminum has a much higher affinity for negatively charged surfaces such as soil and can be taken up in solution easier and is more bioavailable (Lawrence and Huntington 1999). Decreased concentrations of calcium may also be the result of calcium leaching from the root zone via cation mobilization (Bondietti et al. 1990). Likens et al. (1996) estimated that acid deposition might have caused a 50% decline in calcium in soil during the past 45 years in the northeastern United States.

The cation exchange capacity (CEC) of wood decreases as a tree ages (Momoshima and Bondietti 1990). Momoshima and Bodietti (1990) concluded that the calcium binding capacity of wood is highest near the pith and decreases toward the cambium along the radius of the tree. While aluminum and calcium concentrations are affected separately, ratios of aluminum to calcium are used to normalize these declines in concentration and are more representative of nutritional chemistry (Bondietti et al. 1989). These ratios may also be used as an indicator of growth stress caused by toxic chemicals. High Al:Ca ratios found in soil solution may correspond to high Al:Ca ratios in tree rings, which could indicate the interference of calcium uptake by aluminum.

Bondietti et al. (1989) found that declines in radial growth after 1940 correspond with increased Al:Ca ratio in red spruce in the Great Smoky Mountains National Park. Red spruce and eastern hemlock cores sampled showed a statistically significant inverse relationship between radial growth and changes in Al:Ca ratio. This suggests that increased aluminum availability correlates with decreased radial growth (Bondietti et al. 1989). Prior to the period of low calcium concentration, there was an increase in the base cation concentrations. Also, tree growth declined sharply and aluminum concentrations increased following periods of increasing divalent cation

concentration. They concluded that there was a statistically significant relationship between trees with reduced vitality and Al:Ca ratios greater than 1.0 in the fine roots.

Red spruce trees growing between 1,620 and 1,670 meters on Whitetop Mountain in Virginia were fertilized with calcium, magnesium, and nitrogen to determine nutrient deficiencies (Joslin and Wolfe 1994). Fertilization resulted in increased foliar concentrations of calcium and magnesium, indicating that the trees were calcium-limited before the application. Based on these results, it appeared that poor root uptake of calcium was due to the low availability of base cations in the soil.

Mobilization of calcium and magnesium in soil solution will appear as increased uptake; however, the excess cations could eventually leach from the soil or become displaced by another element, such as aluminum. Shortle et al. (1997) compared the concentrations of calcium and magnesium in growth rings of trees and soil in 12 northeastern United States locations. They concluded that concentrations of calcium and magnesium increased in wood formed during the 1960s, which was a period of increased nitrate and sulfate deposition. Shortle et al. suggested that following this increase of base cations; mobilization of aluminum would eventually displace and hasten the loss of calcium and other essential cations from soil.

A decline in calcium concentrations was found during the mid 1900s in red spruce at Camels Hump, Vermont, and the Great Smoky Mountains National Park. Bondietti et al. (1990) reported that growth rate decreased after 1980; these declines corresponded to a decline in calcium concentration.

Presence of Lead in Tree-Rings

Lead is found in the earth's crust and in rocks; however, much of the lead available in the environment is the result of human activity. Leaded gasoline, mining, and the burning of fossil fuels are all examples of how lead may be released into the atmosphere. Trees may absorb heavy metals, such as lead, in sapwood via ion displacement. Lead concentrations in woody tissues, commonly observed in gymnosperms range from 0.9-13 ppm (Adriano 1986). Bindler (1999) believed foliar uptake is the predominant source of atmospheric lead uptake in trees; however, many researchers have observed root uptake of lead from soil solution. Lead concentrations in agricultural soils range between 2 and 200-ppm lead; however, lead concentrations in soils

remote from human activity range from 5 to 25 ppm. Lead found in soil accumulates on the surface and continues to decrease in concentration with depth (Adriano 1986). Lead within the soil undergoes hydrolysis below pH 6 and binds with clays in soil through adsorption. If lead is present in soils with low pH, the lead can compete with other ions in the soil for the exchange sites in root systems. This increased acidity of soils may facilitate root uptake of lead in solution (Forget and Zayed 1995). Using clay soils, Bittel and Miller (1974) showed that lead was preferentially adsorbed over calcium.

Herrick and Friedland (1990) reported that increased lead concentrations on the forest floor of Green Mountain in Vermont and the White Mountains of New Hampshire correlate with acidic soils. The pH in soil cores from 2 areas was low and lead concentrations were high. Bryophytes in the Green Mountains also had high concentrations of lead. The acidity of the soil may have mobilized lead resulting in uptake by tree roots.

Zechmeister (1993) looked at the concentrations of heavy metals in mosses collected on 5 mountain ranges in the northern and eastern Alps. Lead concentrations increased with rising altitude. He attributed the high amount of lead found at greater elevations to high levels of precipitation.

Guyette et al. (1991) observed that lead and cadmium concentrations increased over time in the xylem of trees growing in the mining district of southeast Missouri. Lead and cadmium concentrations reached 11 $\mu mol\ kg^{-1}$ in trees growing in acidic soils ($pH<4.6$), but did not increase in trees growing in control sites ($pH>5$). Lead and cadmium are soluble in acidic soil due to the low pH; therefore, higher metal concentrations in soil solution are expected in low pH soils.

Leaded gasoline used in automobiles during the mid-twentieth century may have been a source of lead deposited in soil. Rolfe (1974) evaluated lead concentrations in sugar maple, northern red oak, and loblolly pine (*Pinus taeda* L.*)* at 3 locations in Champaign, Illinois. Two of the sites were located near heavily traveled highways and the third or control site was further away. Lead concentrations in tree rings increased during the last ten years of growth at the 2 sites sampled at 10 and 30 meters from roadways. Lead concentrations did not increase in tree rings at the control site.

Kardell and Larsson (1978) used the annual growth rings of trees in Stockholm, Sweden, to determine if variable exposure to lead and cadmium over the course of time would be reflected in the corresponding rings. They noted an increase in lead after 1950 in trees growing adjacent to a road. They concluded that these results demonstrated a correlation between lead concentrations and the increase in traffic during the 1950s.

Beech Bark Disease

Beech bark disease is the result of two organisms working antagonistically on the health of American beech trees. The beech scale (*Cryptococcus fagisuga)* insect invades the bark of the tree where it appears as a white "wool-like" wax and is 0.5 to 1.0 mm^3 long (Houston and O'Brien 1983). The insect attacks by inserting its mouthpart, a needle-like stylet, into the bark of the tree, extracting sugars and other nutrients (Houston and O'Brien 1983). The beech scale population is made up entirely of females, which lay eggs and produce larvae. The wingless larvae, also known as the crawler, are wind disseminated to other beech (Houston and O'Brien 1983).

The wounded sites left by the beech scale become susceptible to invasion by the *Nectria* fungi. Damage by the fungi can only occur after the presence of the beech scale. There are two fungi associated with the disease, *Nectria coccinea* var*. faginata* and *N. galligena* (Skelly et al. 1987). The fungi produce two types of spores, asexual, which appear as white wool in the summer and sexual spores that are bright red fruiting bodies (Skelly et al. 1987). The beech scale along with the fungi eventually kills sections of inner bark causing cankers that can girdle and kill the tree (Houston and O'Brien 1983). Symptoms of the disease first appear as the white dots of wool on the bole of the tree. Some trees exhibit "tarry ooze" from spots of dead bark while others form large reddened areas of infection (Houston and O'Brien 1983).

There are several predators and parasites that partially control beech scale and Fungi. The ladybird beetle (*Chilocorus stigma)* is the most common predator that feeds on the scale; however, it does not feed on all life stages (Houston 1996). The mycoparasite, *Nematogonum ferrugineum,* parasitizes the *Nectria;* however, the effectiveness of these organisms for controlling the disease needs further evaluation (Houston 1996).

This disease was imported from Europe to Nova Scotia in 1890. It is now found in Maine, Massachusetts, New York, New Jersey, Pennsylvania, West Virginia, the Great Smoky Mountains in Tennessee, and has been noted in Highland and Rockingham Counties in northwest Virginia (Tim Tinger, personal communication 2000). The beech bark scale and fungi were not found in Smyth, Grayson, and Wythe counties in Virginia at the time of the study.

While beech bark disease has not yet been found on Mount Rogers or Whitetop Mountain, it is important to note that an insect attack by bark scales and fungi can act as a contributing factor to decline of a forest ecosystem already predisposed to stressors that have weakened the tree. McLaughlin (1985) points out that stresses like insect defoliation and damage can alter the physiologic condition of the tree, making it more susceptible to secondary biotic stresses. If the health of a tree is already in a state of decline due to nutritional deprivation caused by aluminum or lead mobilization, then onset of insect attacks may further degrade tree health.

Local Industry

Local industry could play an important role as possible sources of air-transported pollutants. The town of Saltville, Virginia, located 40 km northwest of Mount Rogers and Whitetop Mountain, contains the remains of the Saltville Disposal Ponds, a national Superfund site declared by the Environmental Protection Agency -CERCLIS No. VAD003127578 (Walters 1987). The Mathieson Chemical Corporation/Mathieson Alkali Works operated from 1895 to 1950 producing commercial bleaching powder and chlor-alkali products (Saltville Website 2000). In 1914, Mathieson Alkali Works established the Nitrogen Products Company plant to produce two forms of cyanide, sodium ferrocyanide and sodium cyanide, for military use (Smyth County News & Messenger 2001). Chemical Plant No. 4 was built in Saltville by the Chemical Warfare Service Department of the United States and continued in operation until 1923 (Smyth County News and Messenger 2001).

The Olin Corporation purchased Mathieson Alkali Works in 1950 and it operated until 1972. During this time an electrolytic chlorine and caustic soda plant operated and subsequently released an estimated 100 pounds per day of mercury into wastewater ponds located onsite (Walters 1987). Other contaminants reported in the Agency for Toxic Substances and Disease Registry's Public Health Assessment for the Saltville Waste Disposal pond include cadmium,

lead, and arsenic. In 1974 the plant was demolished and remediation efforts were proposed (Walters 1987).

Lead was mined from the Austinville Mines in Wythe county Virginia, 65 km northeast of Mount Rogers from 1750 to 1981 (BPJ 2000). During the 1800s, a majority of the lead mined in this area was transported to a lead shot tower that was constructed early in the 1800s. The shot tower operated to make ammunition used in firearms for the settlers and later during the Civil War (State of Virginia Website 2000). An estimated 3 million pounds of lead was used during the civil war at this shot tower (Smyth County News and Messenger 2001).

CHAPTER 3
METHODOLOGY

Mount Rogers National Recreation Area: Site History and Characteristics

Mount Rogers National Recreation Area, which is located in southwestern Virginia, covers 120,000 acres (USFS MA15 2000) and includes Whitetop Mountain and Mount Rogers. Settlement near Mount Rogers began around 1740 and the area was legally opened through Indian treaties after the Revolutionary War (Pyle and Schafale 1988).

The U.S. Spruce Lumber Company began the first logging operations on the northeast side of Mount Rogers in 1905. It was during this period that railroads and mills were constructed in the area to remove logged products (Pyle and Schafale 1988). Eventually the area south of Mount Rogers was logged to fulfill an increased demand for lumber during World War I. Logging continued on Mount Rogers until the 1960s (Pyle and Schafale 1988). It is estimated that 50,000 to 100,000 board feet of timber per acre was removed from the northern sides of Mount Rogers during this time (Pyle and Schafale 1988).

The summit of Whitetop Mountain consists of a grassy bald, with spruce trees near the top. During the mid to late 1800s cattle grazed Whitetop Mountain, and Wilburn, Cabin, and Briar Ridge on Mount Rogers (Saunders 1979). The red spruce on Whitetop Mountain were spared from cutting because of their small size; however, logging of hardwoods began in 1909 by the Hassinger Lumber Company and continued through 1921. A hotel, other accommodations, and a road to the summit of Whitetop were built in 1897; the hotel was removed in 1971 (Saunders 1979). There are no other established buildings on the summit of Whitetop Mountain with the exception of Federal Aviation Administration (FAA) communications equipment and Tennessee Valley Authority (TVA) equipment. Portions of the Appalachian Trail were cut through Mts. Rogers and Whitetop and in 1966 both were dedicated as a National Recreation Area managed as the Jefferson National Forest (Saunders 1979).

Site Characteristics

Research plots were established in areas considered to be representative of the northern hardwood forest. Dominant tree species found within the plot areas included sugar maple, red maple, buckeye (*Aesculus pavia* L.), yellow birch, and American beech. Dominant understory found on a majority of areas includes blackberry (*Rubus canadensis* L.), ferns, *Rhododendron catawbiense* Michx., sedges, Hobblebush (V*iburnum alnifolium* Marsh.), and various seedlings. The soils of Mount Rogers and Whitetop Mountain are Typic or Pachic Haplumbrepts and the greater part of parent material consists of rhyolite (Joslin and Wolfe 1992). The area receives around 130 cm of annual precipitation, with an mean rainwater pH of 4.2; in addition there is 10 to 50 cm of cloudwater deposition, mean pH=3.5. Joslin and Wolfe (1992) report that 32% of the time, the forest is enshrouded in clouds. The mean annual temperature is 7°C with a relative humidity of 86% (Joslin and Wolfe 1992).

Establishment of Research Plots

24 research plots were established June through August 1999 as part of a TVA/USDA Forest Service research project designed to collect baseline data for future evaluation of northern hardwood forest health (Figure 1). A subset of the TVA / Forest Service plots were used for the dendrochemical analysis. 16 plots with American beech were chosen within a desired macro aspect (northeast, northwest, southeast, or southwest) at elevations of 1,371m and 1,524m with a +/- 30.5m allowance for determination of plot location (Figure 2). Appendix A contains information pertaining to the research plots used for the dendrochemical analysis. Directional azimuths were randomly chosen between 0-359 and drawn from the tops on Mount Rogers and Whitetop Mountain on topographic maps. Plots were established on sites with less than 50% slope. Site measurements included elevation, aspect, percent slope, and location recorded with Global Positioning System (GPS). Plots were laid out along the contour of the mountain in 2-meter by 2-meter grids using two 30-meter fiberglass measuring tapes along the bottom and right-hand side of the plot and a 50-Meter tape running along the top and left-hand side of the plot following methods described by Zedaker and Nicholas (1990).

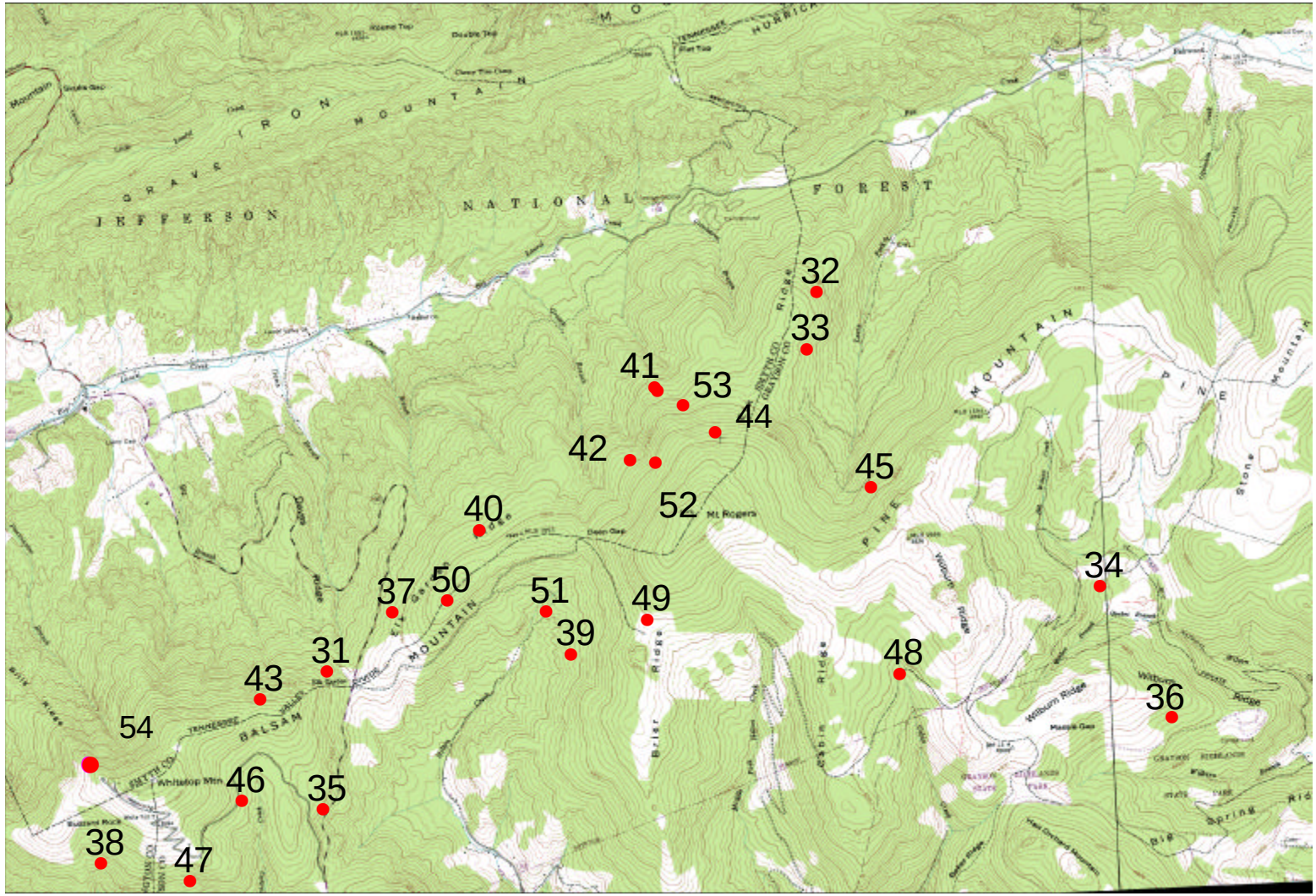

Figure 1: TVA/US Forest Service research plots established on Mount Rogers and Whitetop Mountin, Vriginia in 1999, N=24. (Portions of Whitetop and Trout Dale 7.5 Minute topograhic quadrangle maps)

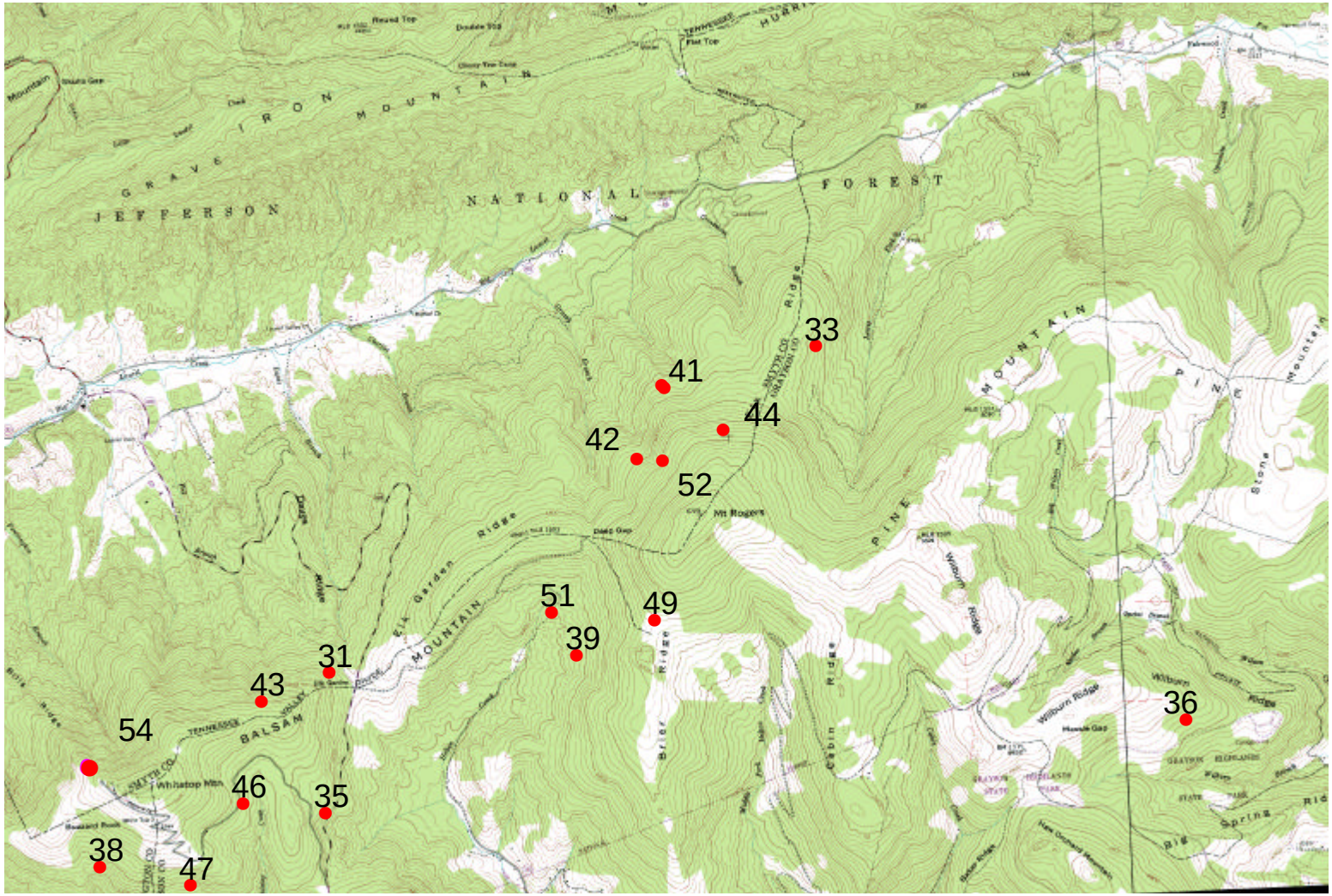

Figure 2: Research plots on Mount Rogers and Whitetop Mountain, Virginia used in dendrochemical analysis, N=16. (Portions of USGS Whitetop and Trout Dale 7.5 Minute topographic quadrangle maps)

The first 10 trees with a dominant or codominant crown position, beginning at the bottom left-hand corner of the plot, were cored for age determination. American beech trees included among the 10 selected trees were included in this study. Dominant trees were defined as having crowns that extend above the general level of the canopy and receive light from above with partial light from the sides. Codominant trees are made up of a crown that is within the general level of the canopy and receives full light from above, with little light from the sides (Zedaker and Nicholas 1990).

Tree cores were collected at 8 plots at an elevation of 1,371 m and 8 plots with an elevation of 1,524 m. A total of 30 trees were used for the analysis. The tree cores were sampled at right angles 15.24 cm below diameter at breast height (1.37 meters above the ground) using a 5.15 mm increment borer. Incremental borers were tested for contamination by rinsing the equipment in a 10% nitric acid solution for examination on an atomic absorption spectrometer. Each sample was individually placed within plastic drinking straws for transportation and labeled with plot, species, and tree number. Samples were immediately stored in a freezer until arrival at the laboratory where they were stored until mounting and placed in a 4°C refrigerator to prevent moisture, causing the wood to swell and mold to form.

Sample Processing for Dendrochronology Analysis

Mounting consisted of drying samples on low setting in a microwave oven (Panasonic, model # NE-6560A, Matsushita Appliance Company, Secaucus, New Jersey) for 30 seconds to prevent mold growth on the sample; a beaker of water was placed in the microwave unit to prevent samples from warping (N.S. Nicholas, personal communication 1999). The cores were glued into a slotted clear pine mount with Elmer's Carpenter's Glue (Elmer's Products, Inc., Columbus, Ohio) and secured by placing an additional piece of wood on top and fastened using elastic bands. Samples were allowed to dry overnight. The mounted cores were sanded down with 240, 400, and 600-grit sandpaper and polished with 1500-grit sandpaper to view the rings with more precision.

Measurement of Ring Widths

Core samples were read from the bark end of the sample to the pith using a Banister Incremental measuring device (Acu-Rite Company, model # 380720, Jamestown, New York). Growth rates of the tree samples were taken by measuring to the 0.001 mm. Samples were placed on an Acu-Rite Mini-Scale Turn Mate/ Mill Mate (Acu-Rite Company, Jamestown, New York) where the core slowly passed under a 10x stereoscope fitted with a 13.6x Javelin Color Camera model JE3462HR, which projected the image on a television monitor. An Acu-Rite 111 digital readout system was used to transform the measurements from analog to digital format into a Gateway 2000 4DX-66V Computer. Ring width measurements were read using the Turbo Ring Read Program, (Van Deusen 1988) converted into Tuscan format and crossdated using the software program COFECHA (Dendrochronology Program Library, Richard Holmes, ANSI Standard Fortran-77, 1986, Laboratory of Tree-Ring Research, University of Arizona; Tucson, AZ) that is part of the International Tree Ring Data Bank Library (Grissino-Mayer et al.1992).

Crossdating

COFECHA was designed to check for measurement errors of ring widths, including missing and double rings and to verify crossdated years. The program was developed to identify yearly segments of tree-rings, which do not correspond to the normalized pattern of ring widths found in all trees sampled from an area close to one another. The entire tree core sample was checked by dividing it into segments of several years. The program checked the tree ring segment widths and flagged areas that weakly correlated with the mean width patterns of all tree cores in the data. For the segments that differed significantly, COFECHA calculated correlations for segment positions differing from the year originally examined. This occurred by shifting the segment position plus and minus 10 years from the original segment. If a correlation was higher at another dated position, the tree core sample was re-examined in that particular area to check for missing or double rings.

Standardization

Ring measurements used to model growth according to climate variables were standardized to remove age-related growth using the computer program, ARTSAN, created by the International Tree Ring Data bank. Age-related growth is influenced by stand competition and disturbance. When the tree is in the juvenile stage it will put on a greater volume of wood each year increasing the bole radius, but as the tree ages it tends to follow a negative exponential growth curve (Cook and Kairiukstis 1990).

To account for this occurrence, ARSTAN standardizes the data by fitting the raw ring width data with a negative exponential regression line. The modified negative exponential curve (Equation 1):

$$Y = A^* e^{(-B * t)} + D \quad (1)$$

was selected from the program and fit to the data. Fitting the curve to the width data removes the signal associated with age variability and stand competition so that it does not mask the width that is actually the result of climate/exogenous influences. The process of standardization transforms the nonstationary ring widths into index values that are stationary and have a defined mean of 1.0. Index values were created by dividing the raw ring measurements by the trend line. The resulting transformation is a growth curve that is "free" of age related trends. Ring width indices were calculated for each year and then averaged by year to produce an Arstan master chronology for the total of all trees.

Sample Processing for Dendrochemical Analysis

30 duplicate samples used in the aging process were also used for the dendrochemical analysis. All tree cores were sectioned into ten-year growth periods by shaving the top layer of wood from the core with a stainless steel razor blade and comparing samples used for chemical analysis with crossdated samples under a 10x stereoscope. The 10-year ring sections were then separated with a stainless steel razor blade. Core sections were weighed and dried in an oven for 48 hours at 50°C until constant mass was achieved. Samples were then pulverized in a stainless steel Wiley Mill with a 20-mesh filter at the TVA Public Power Institute's Environmental Impact & Reduction Technologies laboratory in Norris, Tennessee. Personal protective equipment was

worn during sample processing and quality control measures were taken to avoid sample contamination.

Acid Digestion

Samples were prepared for atomic absorption spectroscopy using a nitric acid/30% hydrogen peroxide digestion technique. Digestion techniques followed a protocol for digestion of soils, sediments, and sludges described in the United States Environmental Protection Agency: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846. Version 111A. Tree core samples, ranging from 0.014 to 0.274 grams were digested in 10 mL of 1:1 nitric acid on a hot plate and refluxed to 5 mL without boiling. Five mL aliquots of nitric acid were added to the sample until the digestion was complete. Digestion was considered complete when the sample reached a stable light color, absent of dark fumes. Two mL of water and 3 mL of 30% hydrogen peroxide were added and additional 1 mL aliquots of hydrogen peroxide were added until effervescence ceased. Final sample volume was adjusted to 100 mL with de-ionized water and the diluted sample was vacuum filtered through a Whatman No. 41 filter paper.

Lead, Aluminum, and Calcium Quantification

Tree core samples were analyzed for aluminum, lead and calcium using a Varian Atomic Absorption Spectrometer (Varian Spectra AA-10/20, GTA 96. Varian Techtron Pty. Limited, Victoria Australia) equipped with a flame aspirator and a graphite furnace. Certified aluminum, lead, and calcium standards from Fisher Scientific (Lead CAS# 1009-74-8, Aluminum CAS# 7647-01-0 and Calcium CAS# 471-34-1, Fisher Scientific, Atlanta GA) were used to make all standard solutions. Standard solutions for atomic absorption analysis were prepared in a separate room from the instrument to prevent instrument and sample contamination. Initial instrument calibration was carried out using 5 working standard solutions. Analyses of aluminum, lead, and calcium were conducted separately. All methods follow the United States Environmental Protection Agency: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846. Version 111A. Methods are presented in Appendix B. Interference with sample matrix was avoided by adding a matrix modifier to each sample, standard, and quality control sample used for the corresponding analysis. Potassium nitrate was added in 0.2-µL aliquots per sample for

aluminum analysis; 2-µL of nickel nitrate was added for lead measurements; and 1-ml of lanthanum chloride solution was added per 10-ml sample for calcium quantification.

The furnace method was used to determine concentrations of lead in tree-ring samples because expected concentrations were at the µeq g^{-1} level. Aluminum and calcium concentrations were expected to be at the meq g^{-1} level so the flame method was used. A majority of the samples analyzed for aluminum concentration were determined to be at or below the instrument detection limit (0.1mg L^{-1}). To minimize bias in data analyses the detection limit was used when the reported concentration was below the detection limit. Health and safety information concerning the use of chemicals is presented in Appendix C.

Quality Assurance and Quality Control

Quality control measures consisted of a working calibration curve, including a calibration blank for all cation measurements. The atomic absorption spectrometer was set to check a reference standard after every 10 samples and the reference standard curve after every 20 samples. Quality control samples included a sample spike, blank spike, blank, duplicates, and an unknown certified QA/QC sample (Environmental Resource Associates, Arvada, Colorado) for aluminum, calcium, and lead. A standard reference material of pine needles (1575) from the National Bureau of Standards was used to evaluate the reliability and reproducibility of the atomic absorption (USDOC 1999).

Analysis of Data

Triplicate absorbance readings were used to determine mean absorbance. Concentration calculations were determined directly by the Varian spectrometer based on the standard concentration curve. Concentrations expressed as milligram or microgram of element per gram of tree core material were determined by converting the concentration from mg L^{-1} or µg L^{-1} to mg g^{-1} or µg g^{-1} using Equation 2:

$$\text{Concentration (mg } g^{-1}\text{) or (µg } g^{-1}\text{)} = C*L / \text{grams of sample} \quad (2)$$

Where C is the concentration in mg L^{-1} or µg L^{-1} and L is 0.1L of nitric acid sample extract. Concentrations were then expressed as milliequivalents (meq) or microequivalents (ì eq) to

directly compare the amount of lead, aluminum, and calcium within increment core samples. Concentrations were expressed as chemical equivalents per gram of material using Equation 3:

$$\mu eq\ g^{-1} \text{ or } meq\ g^{-1} = C / meq \text{ or } \mu eq \quad (3)$$

Where C is the concentration (mg g^{-1}) or ($\mu g\ g^{-1}$) of element divided by the meq or μeq. The chemical equivalent was used in the place of mg g^{-1} or $\mu g\ g^{-1}$ in data analysis because it is the weight, which consumes or produces 1 mole of electrons and gives a better representation of the actual weight for the element (Skoog and West 1969).

Main effects of decade aluminum (Al) concentration, lead (Pb) concentration, calcium (Ca) concentration, Al:Ca ratio, age, aspect, elevation, and interacting terms on total decade ring width were statistically analyzed separately using analysis of variance (ANOVA) tests in SAS Version 6.12 (SAS Institute Inc. 1996). Al, Pb, and Ca concentrations along with age were grouped into classes and also tested for main effects on total decade ring width. All class variables are identified in statistical tests as Pb concentration class, Al concentration class, Ca concentration class, and decade or age class. This term is used to prevent confusion of continuous variables with class variables. The Al, Pb, and Ca concentration data were divided into classes by sorting data in ascending order and grouped based on sample number. Age classes were defined as less than 100 years old, 101-151 years, and >151years. Decade classes were defined by assigning a number to represent 10 years of data within a particular decade, e.g. 1990=1. Decade class numbers and the representative decade values are provided in Appendix D. Tukey's studentized range test (HSD) was used to compare means and determine if differences existed between Al, Pb, and Ca concentrations, width, and elevation effects. The general linear model procedure (GLM) was used for unbalanced datasets.

The relationship between Al, Pb, and Ca concentrations and total decade ring width were tested for correlation using the CORR procedure in SAS. The distributions of the means were determined using the Shapiro-Wilks test in the UNIVARIATE procedure of SAS. Total decade ring width was determined to be non-normal at the 99% confidence level and natural log width transformed data were used for analysis of variance. Lead, aluminum, and calcium concentration values were ranked because they were non-normal. Spearman correlation was used for the for the correlation analysis between cation concentrations and ring width.

Cation concentrations were examined through time. Lead, aluminum, and calcium concentration data were indexed given that all trees sampled did not span the same time period. This procedure was done to account for the statistical variability that existed between recent decade period data (Guyette and McGinnes 1986) that contained all 30-tree samples and early decade period data from 1740 to 1800 that contained two or fewer samples.
The concentration index (Equation 4):

$$\text{Concentration Index} = \hat{a} * N/T \quad (4)$$

was created by multiplying the average cation concentration (â) for a particular decade by the division of the total number of trees sampled (N) by the total number of trees sampled for the particular decade (T). This procedure gives each decade concentration a different weight that is reflected by the number of samples gathered.

A regression model relating standardized tree-ring widths to monthly climatic variables was developed to model and predict growth according to historical climate data from the National Oceanic and Atmospheric Administration's National Climatic Data Center. Data used in the linear regression are found in Appendix D. The index chronology values for ring widths were determined to be non-normal using the Shapiro-Wilks test in the UNIVARIATE procedure of SAS (99% confidence level). Therefore, Spearman correlation analysis using the CORR procedure in SAS (SAS Institute Inc. 1996) was used to compare index chronology widths to monthly and seasonal precipitation and temperature values. All tests were considered to be significant at the 95% confidence level. Average minimum and maximum temperature values were recorded in the Fahrenheit scale and precipitation was measured in hundreds of an inch. Monthly climate data were considered January through December for a particular year and seasonal data were grouped according to growing season, May through October. Early growing season (May –July) and late growing season (August-October) were also tested. Data from the previous year's growing season, beginning in May, were used as a lag-variable to account for the dependence of current year tree growth on carbon uptake during the previous year's growing season (Grissino-Mayer and Butler 1993). The lag variables were also tested for a correlation with index ring widths.

Regional and local data from four separate weather stations were tested to determine which was the most appropriate for the regression model. The first station, Alexandria Potomac

Yards (Cooperative ID 440097) located in Alexandria, Virginia, is approximately 483 kilometers northeast of Whitetop Mountain. Climate data were collected from this station between 1893 and 1962; however, data from 1905 to 1944 were missing and could not be located by the National Climatic Data Center. Data gathered from the Galax station (Cooperative ID 443267) located 46.7 kilometers east of Whitetop Mountain contained information from 1940 through 1999, Chilhowie (Cooperative ID 441675) 15.3 kilometers due north of Whitetop mountain contained data from 1952 through 1976, and Damascus station (Cooperative ID 442216) located 19.3 kilometers west of Whitetop Mountain contained data from 1931 to 1974. Spearman correlations were calculated for monthly climate variables for each weather station and index widths. Spearman correlations were also calculated for the average precipitation and temperature variables together and for combinations of stations and index widths. The most significant climate variables were determined to be May precipitation from Chilhowie station and Alexandria. These data were used in the regression analysis.

The data were divided into 2 sections; a calibration period of 1945-1970, which was used in the regression model, and a period of 1971-1999 that was withheld from the calibration model to verify climate and growth models produced (Grissino-Mayer and Butler 1993). The time period of 1945-1999 was chosen because of the availability of data. Regression diagnostics using the SAS regression (REG) procedure (SAS Institute Inc. 1996) were conducted. This included the observation of studentized residuals for possible outliers and inspection of Cook's d values influencing regression (Grissino-Mayer and Butler 1993). The model obtained was:

$$R_i = 0.873709 + 0.03 * P_i \quad (5)$$

where R_i was the predicted index for year i and P_i was the precipitation average. The residual growth data from the predicted climate model were then compared with the predicted growth values to determine if there were growth anomalies due to factors other then climate influence growth.

CHAPTER 4
RESULTS

Cation Concentrations and Tree Growth

Using Spearman correlation coefficients, a significant negative relationship ($p<0.01$) between total decade ring width and cation concentrations or Al:Ca ratio was determined (Table 1). An analysis of variance (ANOVA) using general linear models (GLM) indicated that variability in lead and aluminum concentrations, plus the Al:Ca ratio explained some of the variability in tree-ring width (Table 2). Calcium concentrations and interactions among concentrations did not.

An analysis of variance on ring width indicated a high statistical significance for lead concentration class (Table 3). Mean ring widths per decade decreased in size as lead concentration classes increased; however, width did not differ significantly until the ring width that corresponded with concentration class 1 (defined in the method section) was analyzed using Tukey's studentized range test for contrast among means (Table 4). Using ANOVA on ranked lead concentrations the age class of a tree sample was found to be significant (df= 2, *F* value=16.66, α=0.01). Decade values, in addition to decade class values, were not statistically significant for ring width.

Variability in ring width was associated with variability in aluminum concentration classes (Table 3). Mean ring width decreased in size as aluminum concentrations increased with the exception of concentration class 6, which had the smallest average width (Table 5). The age of the tree was statistically significant for the width of the total decade ring width (*F* value=4.61 α=0.05). Age class, decade class, and decade values were not statistically significant for ring width.

Ring width was significantly associated with variability in calcium concentration class (Table 3). Concentration class 1, the lowest calcium concentration class, was significantly different than all other concentration classes; in addition, average tree-ring width was highest for this category (Table 6). Tree age was only slightly associated with ring width (*F* value=3.75 α=0.05). Out of the 300 decade samples analyzed for the 30 trees cored, only 8 decade samples

Table 1: Comparison of total decade ring width with lead, aluminum, calcium concentration and Al:Ca ratio using Spearman correlation coefficients.

Source	df	*R* value	Pr> *R*
Lead	298	-0.034027	0.0001**
Aluminum	298	-0.067776	0.0001**
Calcium	298	-0.38888	0.0001**
Al:Ca Ratio	298	-0.16025	0.0056**

**Indicates significance at 0.01 confidence level

Table 2: Analysis of variance (ANOVA) of tree-ring widths† for the main effects of lead, aluminum, calcium concentrations, and the ratio of Al:Ca.

Source	df	*F* value	Pr>*F*
Pb concentration	1	18.99	0.0001**
Al concentration	1	48.67	0.0001**
Ca concentration	1	1.45	0.2302
Al:Ca ratio	1	16.28	0.0001**
Pb*Al concentration	1	0.58	0.4473
Pb*Ca concentration	1	0.15	0.6974
Al*Ca concentration	1	1.02	0.3128

** Indicates significance at 0.01 confidence level.
† natural log transformed width

Table 3: Analysis of variance of tree-ring widths† for the main effects of aluminum, lead, and calcium concentration class

Source	df	*F* value	Pr>*F*
Pb category	7	5.45	0.0001**
Al category	6	32.91	0.0001**
Calcium category	5	9.82	0.0001**

**Indicates significance at the 0.01 confidence level.
† natural log transformed width.

Table 4: Mean and range tree-ring width (mm) for eight lead concentration classes[1].

Lead Concentration Class	Width			
	Range	Minimum	Maximum	Mean
Class 1	2.622	1.80	2.802	1.325 *b* (0.56)†*
Class 2	1.992	0.500	2.492	1.003 *a* (0.42)
Class 3	1.362	0.356	1.718	0.988 *a* (0.34)
Class 4	1.097	0.479	1.576	0.972 *a* (0.30)
Class 5	1.422	0.551	1.973	0.953 *a* (0.37)
Class 6	1.654	0.248	1.902	0.851 *a* (0.32)
Class 7	2.388	0.391	2.779	0.933 *a* (0.64)
Class 8	1.347	0.296	1.643	0.677 *a* (0.42)

[1] Lead Concentration Class 1 (0-0.0105 µeqg^{-1}), 2 (0.0106-0.021 µeqg^{-1}), 3 (0.022-0.042 µeqg^{-1}), 4 (0.043-0.063 µeqg^{-1}), 5 (0.064-0.084 µeqg^{-1}), 6 (0.085-0.168 µeqg^{-1}), 7 (0.169-0.252 µeqg^{-1}), 8 (0.253-0.336 µeqg^{-1}).

NOTE: Mean tree-ring width values followed by the same letter are not significantly different (p=0.05) based on Tukey's studentized range test for comparisons among natural log transformed values

† Values in parentheses represent the standard deviation.

*Represents data significant at 95% confidence level

Table 5: Mean and range tree-ring width (mm) for aluminum concentration class[1]

Aluminum Concentration Class	Width			
	Range	Minimum	Maximum	Mean
Class 1	2.401	0.401	2.802	1.745 *a* (0.60)†
Class 2	1.600	2.654	0.754	1.395 *b* (0.35)
Class 3	0.956	0.519	1.475	1.019 *c* (0.22)
Class 4	1.623	0.180	1.803	0.917 *d* (0.27)
Class 5	1.706	0.391	2.097	0.822 *d* (0.32)
Class 6	1.152	0.248	1.400	0.645 *d* (0.27)
Class 7	1.526	0.425	1.951	0.852 *e* (0.47)

[1] Aluminum Concentration Class 1 (0-0.007 meqg^{-1}), 2 (0.0072-0.010017 meqg^{-1}), 3 (0.010018-0.013 meqg^{-1}), 4 (0.0132-0.015 meqg^{-1}), 5 (0.0152-0.021 meqg^{-1}), 6 (0.0215-0.029 meqg^{-1}), 7 (0.030-0.14 meqg^{-1}).

NOTE: Mean width values followed by the same letter are not significantly different (p=0.05) based on Tukey's studentized range test for comparisons among natural log transformed values.
† Values in parentheses represent the standard deviation.
*Represents significance at 95% confidence level.

Table 6: Mean and range tree-ring width (mm) for calcium concentration class[1].

Calcium concentration class	Width			
	Range	Minimum	Maxiumum	Mean
Class 1	2.135	0.667	2.802	1.391 *a* (.55)†
Class 2	1.801	0.248	2.049	1.055 *b* (.35)
Class 3	1.823	0.180	2.003	1.099 *b* (.46)
Class 4	1.598	0.430	2.028	0.917 *b* (.36)
Class 5	2.196	0.296	2.492	0.871 *c* (.39)
Class 6	1.478	0.401	1.879	0.842 *c* (.37)

[1] Calcium Concentration Class 1 (0-0.025266 $meqg^{-1}$), 2 (0.025267-0.031987 $meqg^{-1}$), 3 (0.031988-0.036427 $meqg^{-1}$), 4 (0.036248-0.042288 $meqg^{-1}$), 5 (0.0429289-0.087048 $meqg^{-1}$), 6 (0.087049-5.57025 $meqg^{-1}$).

NOTE: Mean width values followed by the same letter are not statistically different (p=0.05) based on Tukey's studentized range test for comparison among natural log transformed values.
† Values in parentheses represent the standard deviation.

were found to have Al:Ca ratios greater than 1, the value associated with reduced vigor. The remaining 292 samples did not have values above 1.

Influences of Elevation and Aspect on Tree Growth and Cation Concentration

The variability in elevation and aspect explained some of the variability in total decade ring width (Table 7). Average ring widths per decade were significantly higher at 1,371 meters in elevation than ring widths taken from 1,524 meters (alpha=0.05). Aspect was a statistically significant factor associated with concentrations of lead, aluminum, calcium, and the Al:Ca ratios. However, the variation in elevation only explained statistical variability in lead concentrations. Using Tukey's studentized range tests for comparisons among means (alpha=0.05) mean lead concentrations ($\mu eq\ g^{-1}$) were significantly higher at 1,524 meters than at 1,371 meters. Figures 3 and 4 show the geographic distribution of plots by elevation and aspect.

Mean calcium concentration was highest on northwest facing aspects and lowest on southwest facing aspect (Figures 5). Aluminum concentrations were consistently lower than calcium on all aspects. There was a significant decrease in aluminum concentrations found on southwest facing aspects (alpha=0.05). Mean lead concentrations were highest on southwest and northwest facings (Figures 6). There were significant decreases in lead concentrations found on both northeast and southeast facing aspects (alpha=0.05). Most of the beech trees sampled were between the ages of 40-110 years old (Figure 7).

Climate Influence and Tree Growth

Ring width indices were positively correlated with ($p<0.05$) May precipitation data from Chilhowie/Alexandria stations (Figure 8, Appendix D). These particular weather station data were chosen based on the highly significant relationships between climate variables and ring width indices. Correlations between aspect chronologies, separate Galax and Damascus stations, and seasonal climate groupings were either not significant or not as significant as the Chilhowie data.

An analysis of variance (ANOVA) was run using the average May precipitation data for the years 1945-1999 and yearly tree-ring indices (Table 8). Data were then split into 2 subsets and a linear regression was run on the calibration period of 1945-1970.

Table 7: Analysis of variance for the main effects of aspect and elevation on ring width, aluminum concentration, lead concentration, calcium concentration and Al:Ca ratio.

	Width †			Pb Concentration §			Al Concentration §			Ca Concentration §	
Source	df	*F* value	Pr>*F*	df	*F* value	Pr>*F*	df	*F* value	Pr>*F*	df	*F* value	Pr>*F*
Aspect	3	2.23	0.06 ‡	3	49.47	0.0001**	3	5.11	0.0019**	3	6.57	0.0003**
Elevation	1	11.74	0.0001**	1	53.46	0.0001**	1	1.22	0.2699	1	0.14	0.7101
Aspect*Elev.	3	0.73	0.5361	3	25.90	0.0001**	3	2.43	0.0653‡	3	1.94	0.1238

	Al:Ca ratio §	
Source	df	*F* value	Pr>*F*
Aspect	3	7.90	0.0001**
Elevation	1	1.70	0.1936
Aspect*Elev.	3	6.69	0.0002**

NOTE: df= 1-number of research plots located at the 4 different aspects and elevation established plots.
† Natural log transformed data.
‡ Indicates significance at the 0.10 level.
**Indicates significance at 99% confidence level.
§ Ranked data.

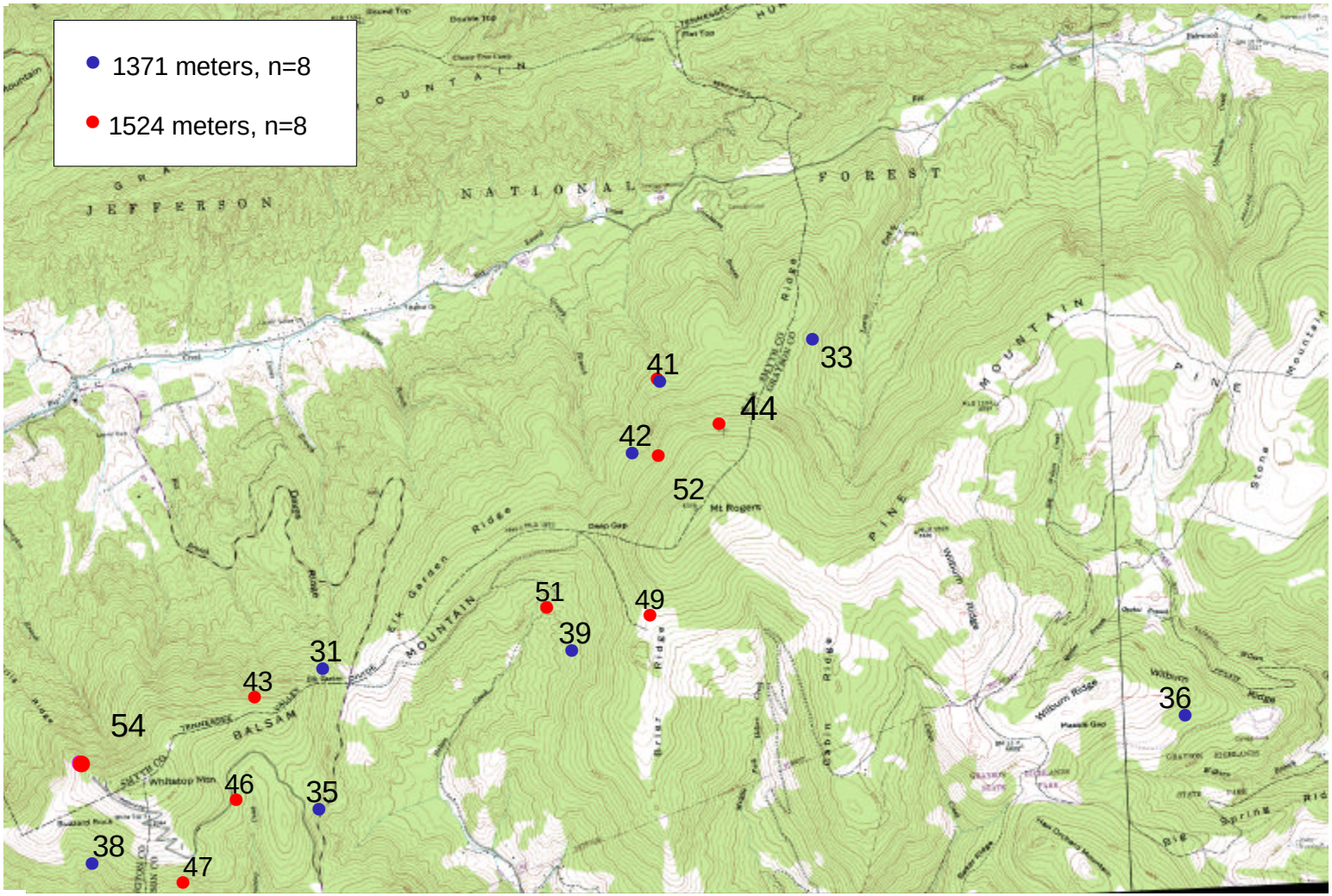

Figure 3: Location of higher (1524m) and lower (1371m) elevation dendrochemical reseach plots. (Portion of USGS Whitetop and Trout Dale 7.5 Minute topographic quadrangle maps)

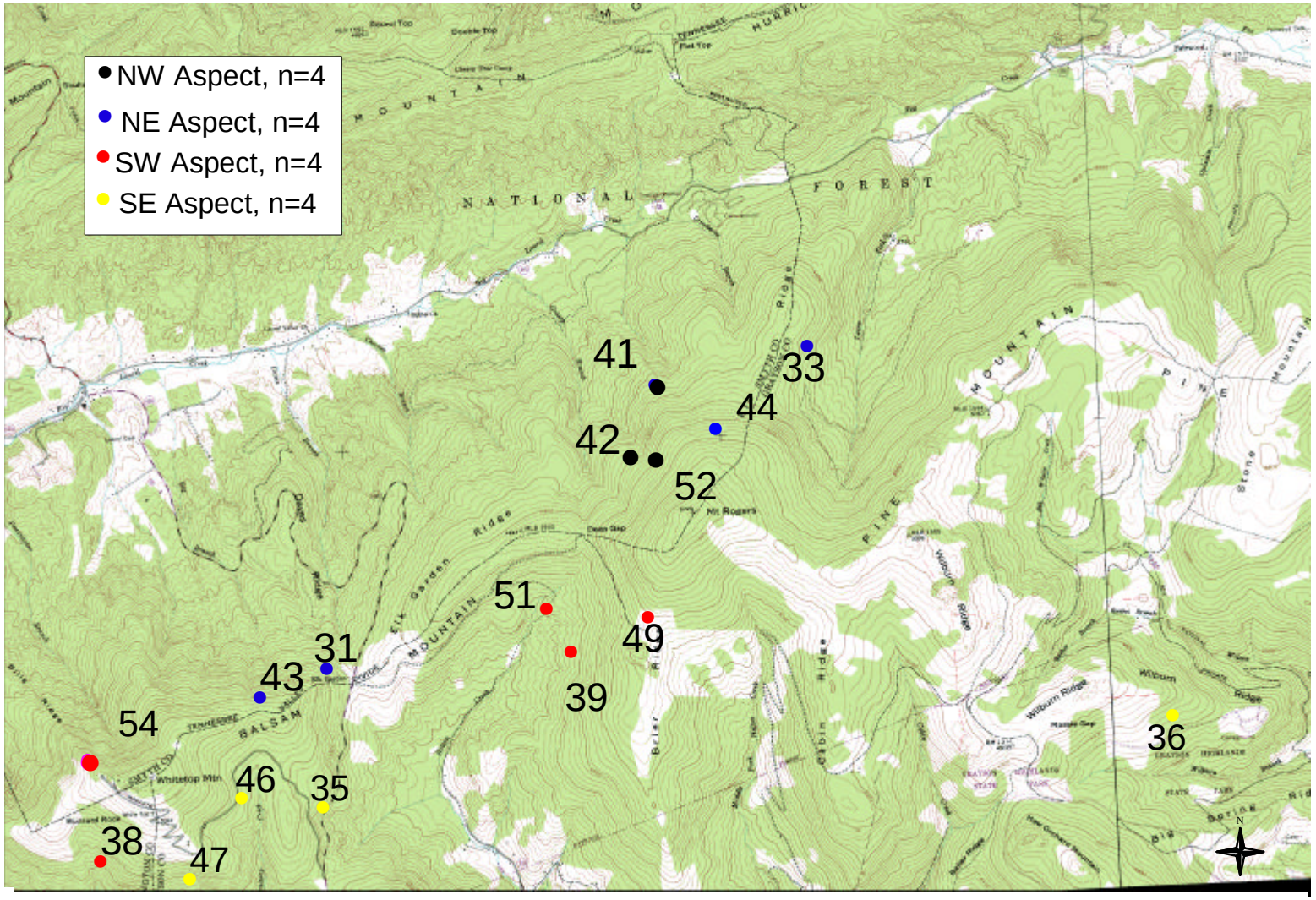

Figure 4: Location of northwest, northeast, southwest, and southeast aspect dendrochemical research plots. (Portion of USGS Whitetop Mountain and Trout Dale 7.5 Minute quadrange maps).

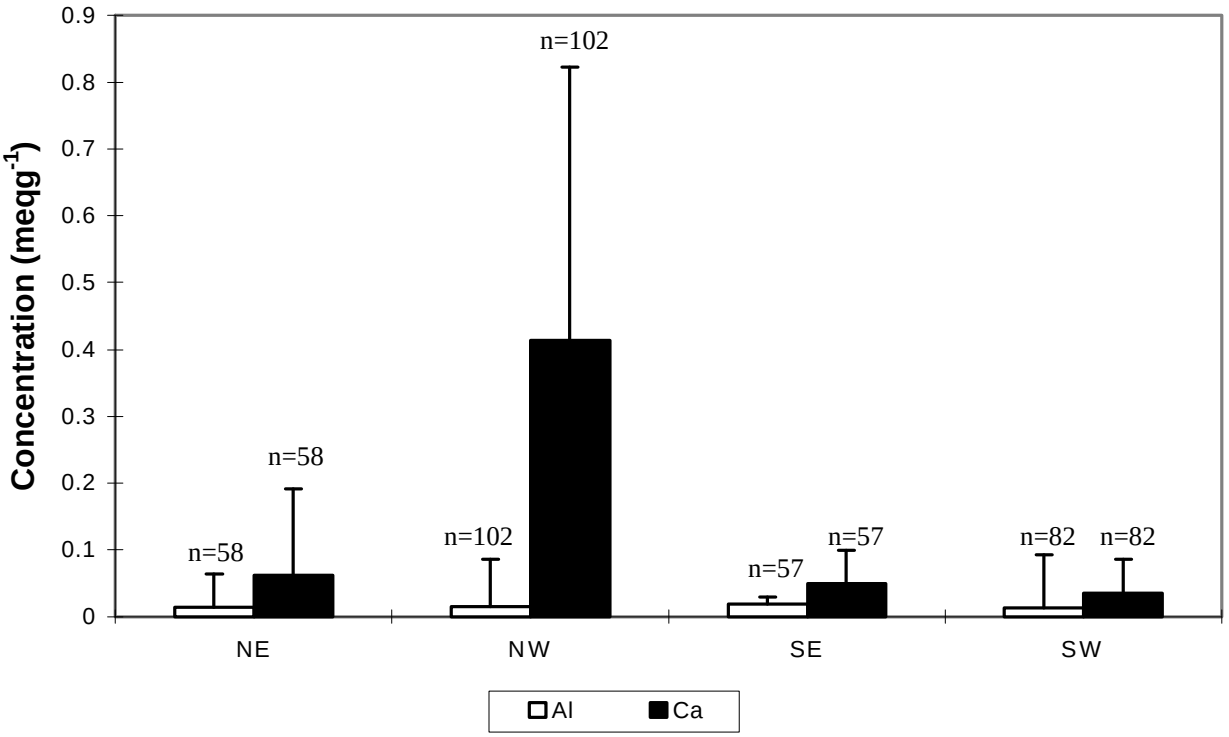

Figure 5: Mean and standard deviation for aluminum and calcium concentrations (milliequivalents per gram of tree sample) of tree-rings at four aspects: northeast, northwest, southeast, and southwest.

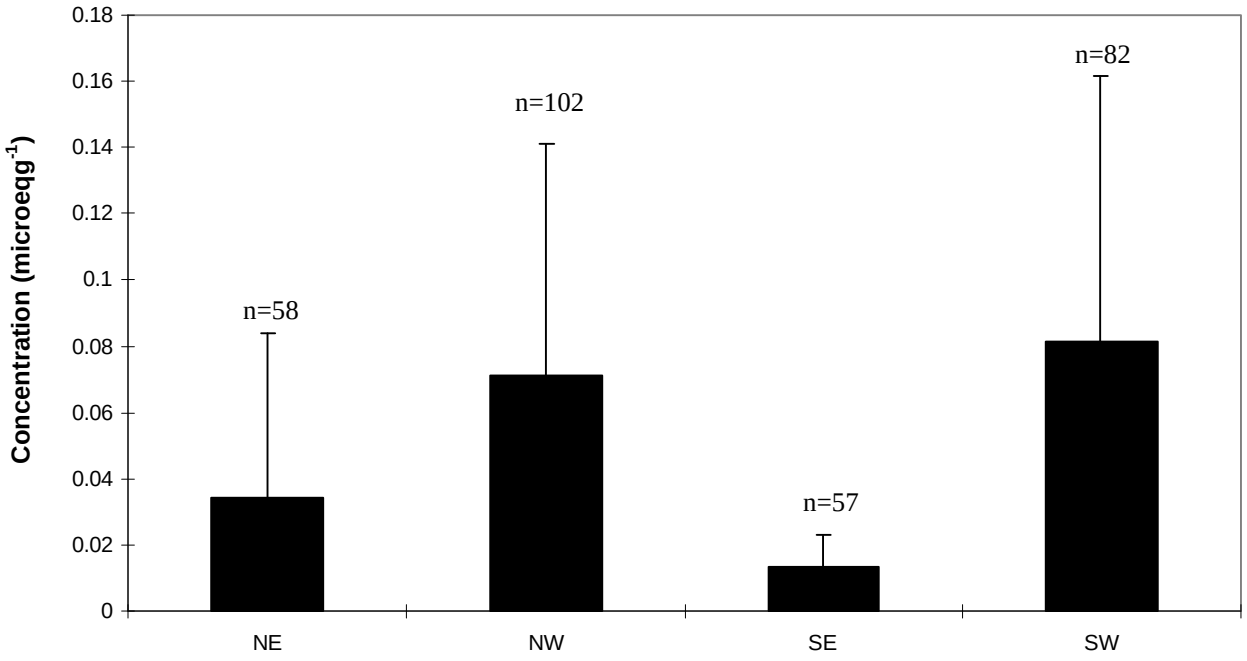

Figure 6: Mean and standard deviation for lead concentration (microequivalent per gram tree sample) of tree-rings at four aspects: northeast, northwest, southeast, southwest.

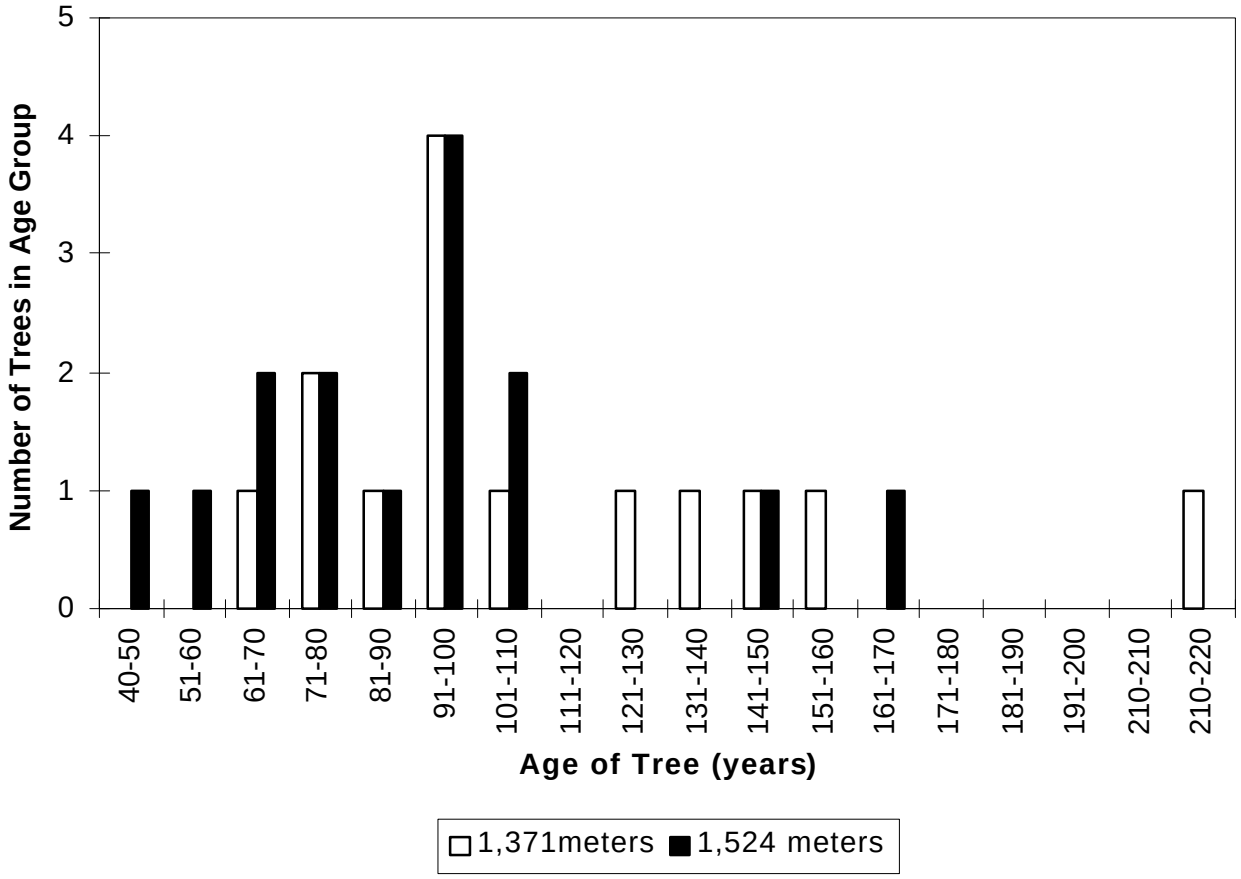

Figure 7: Age distribution of tree samples at 1,371 and 1,524 meters in elevation.

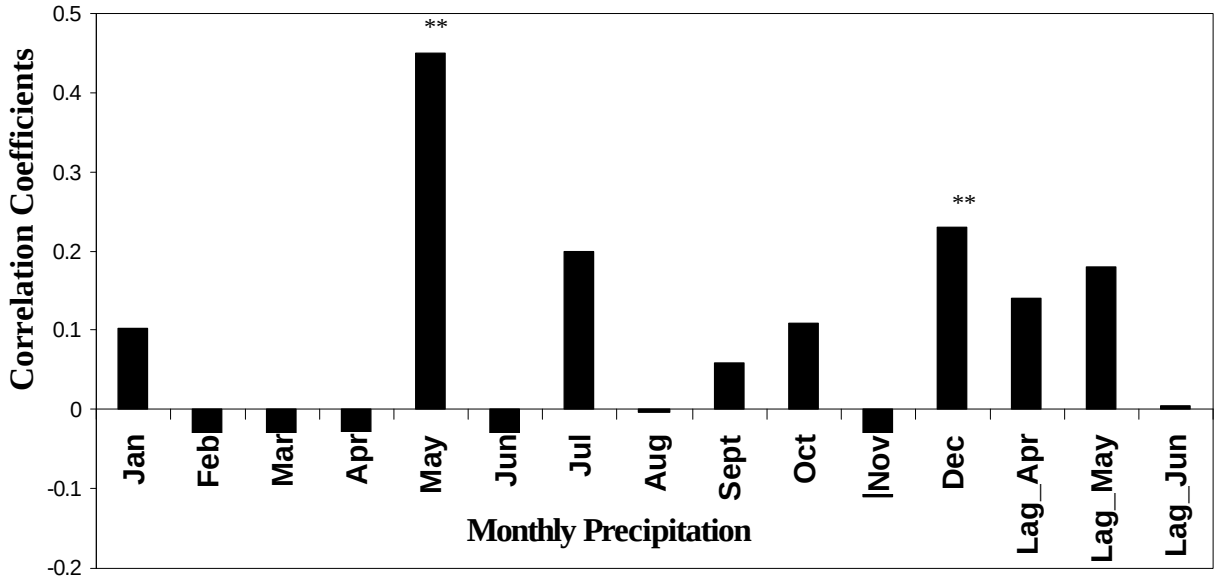

Figure 8: Correlation analysis between Arstan ring-width indices and Chilhowie monthly precipitation (January through December) and previous April, May, and June precipitation lag variables.

**Indicates significant values at the 95% confidence level for Spearman correlation analysis.

Table 8: Analysis of variance (ANOVA) of Arstan chronology ring-width indices for Chilhowie/ Alexandria May precipitation, years 1945-1999 and 1945-1970.

Source	R-square	*F* value	Pr>*F*
1945-1999 precipitation	0.1990	12.67	0.0008**
1945-1970 precipitation	0.3149	11.03	0.0029**
1945-1970 final model	0.439	15.66	0.0008**

**Indicates data at 0.01 confidence level.

Using regression diagnostics 1963, 1969, and 1955 were identified as statistical outliers, based on high values obtained in the studentized residuals and Cook's d values. Data from these years were deleted to remove anomalous climate patterns and provide a better model for climate data. Only growth expected from normal climate variations was used and extreme climate events were removed.

A review of historical climate data indicated that the highest recorded temperature (110 degrees F) for the state of Virginia occurred in 1954 (NCDC 2001). Low precipitation in 1953, high temperatures and low precipitation values during 1954 summer season indicate drought conditions. Records from the Virginia State Climatology Office show that one of the heaviest snowfalls on record occurred during the winter of 1969; therefore, data from 1969 were removed. Historical records indicate that 1963 was one of the driest years on record (Virginia State Climatology Office 2001).

The final regression model was used to calculate the tree growth that would have resulted only from climate influences for the years 1971-1999. The regression model explained 44% of the total variability ($p<0.01$) in the Arstan chronology tree-ring indices (Table 9). The resulting equation (Equation 5) was used to predict growth ring indices for the second half of the data set for years 1971-1999. Actual and predicted yearly index values and their residuals are plotted in Figure 9. Comparison of residuals to predicted growth indices indicated that growth occurring throughout the 1960s was below the predicted values. A sharp decline in the residuals compared to the expected growth also began in 1982 lasting until 1987 (Figure 9). The upper and lower 95% confidence levels for actual and predicted growth-ring indices and May precipitation data are shown in Figure 10.

Cation Concentrations Changes Through Time

Changes in lead concentration were highly variable between individual trees. Therefore, decade averages of all tree samples were used to represent stand level changes. The lead concentration in American beech samples from Mount Rogers and Whitetop Mountain increased from 1740 to 1999 (Figure 11). Concentrations increased beginning in 1900 with an increase again during 1920. Lead concentrations declined in the following decade; however, rose steadily until 1980 (Figure 11). Only 14 samples out of the 300 tree-ring samples processed for

Table 9: Final regression model statistics for precipitation calibration period (1945-1970).

Source	R-square	*F* value	Pr>*F*
May precipitation	0.439150	15.66	0.0008**
Parameter	Estimate	Pr>T	
Intercept	0.8737	0.0001	
May precipitation	0.0273	0.0008	

**Indicates significance a 0.01 confidence level.

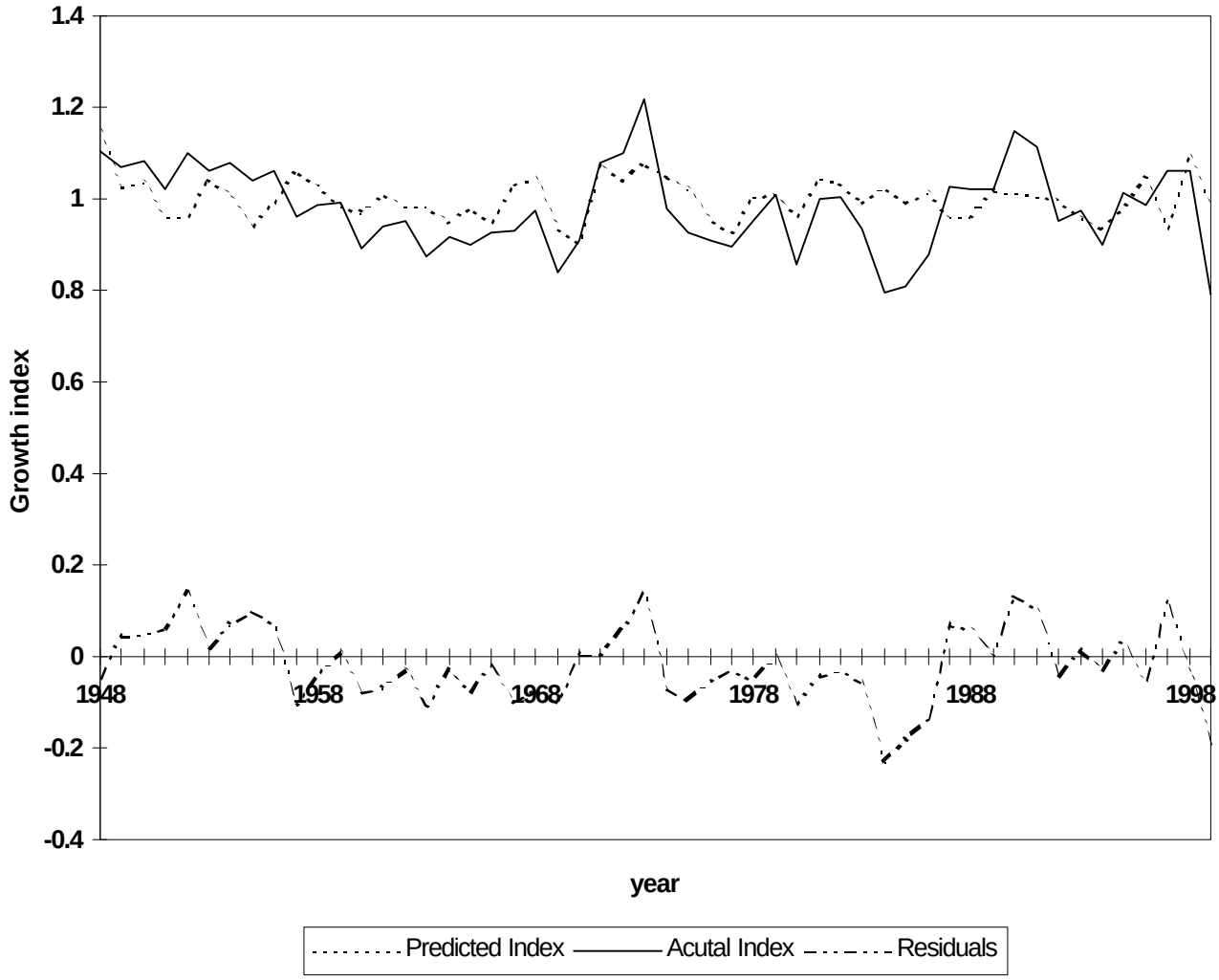

Figure 9: Actual and predicted values of growth ring indices for American beech generated from final regression model.

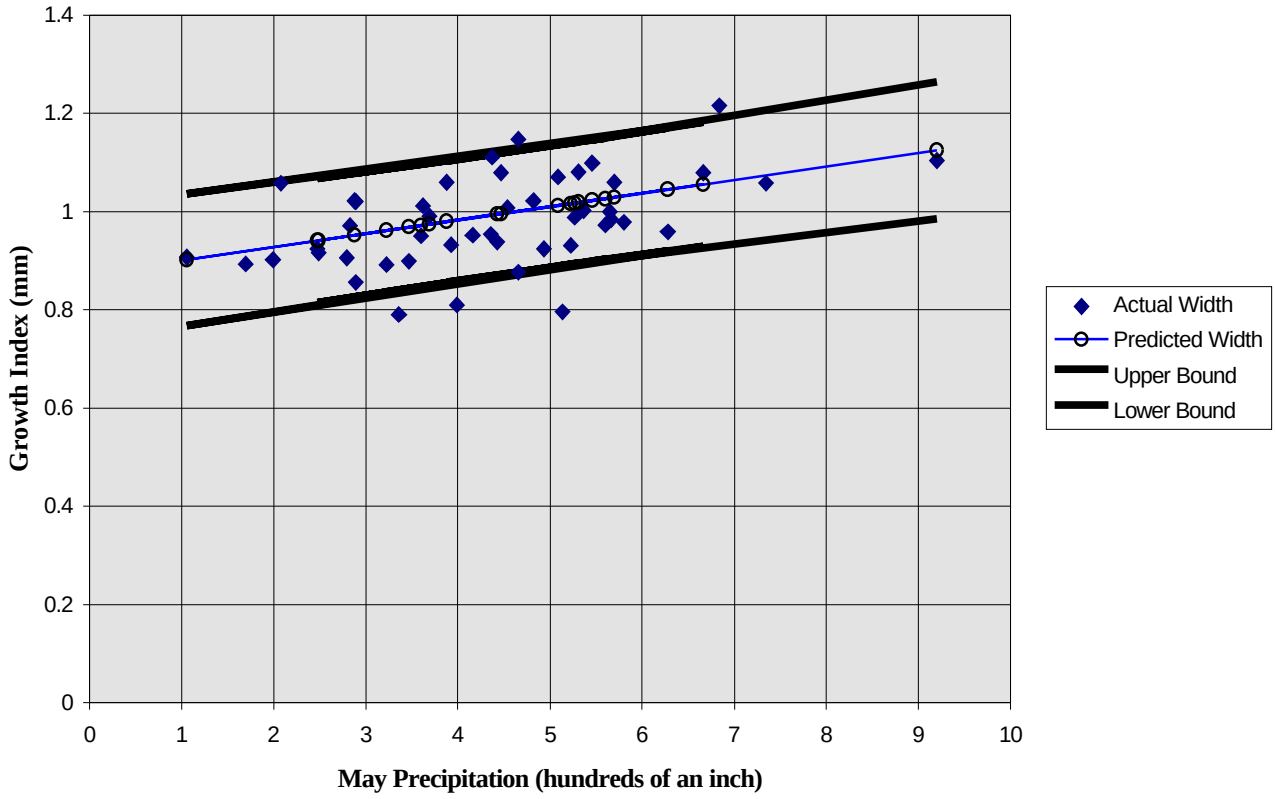

Figure 10: 95% Confidence and prediction bands for growth-ring indices and precipitation data.

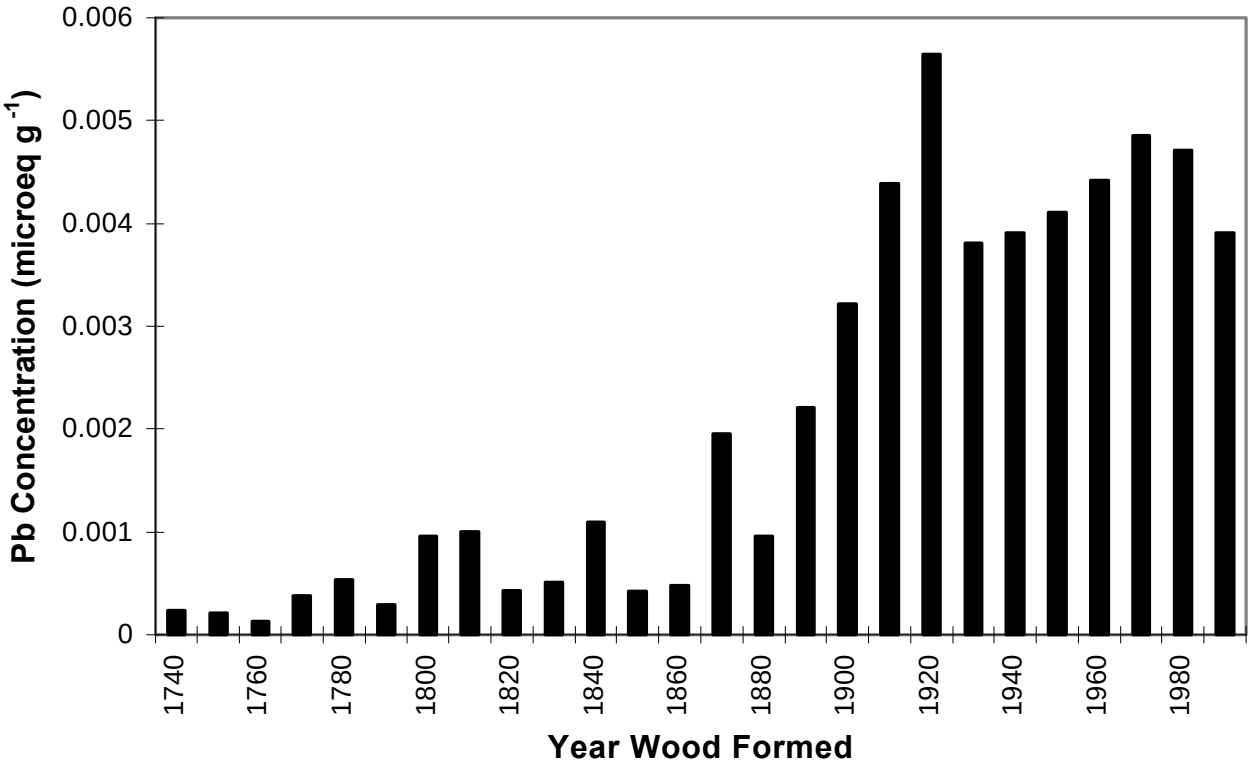

Figure 11: Lead concentration indices through time sampled from American beech on Mount Rogers and Whitetop Mountain, Virginia.

aluminum were above the instrument detection limit of 0.1 mg L^{-1}. Therefore, changes of aluminum concentrations through time were not evaluated.

Changes in calcium concentrations through time in individual trees varied between samples. Concentrations tended to be higher towards the center of the pith for a number of trees, while a few trees showed no unusual concentration patterns elsewhere in the sample. DeWalle et al. (1991) identified calcium as an ion that occurs near both the pith and the cambium of tree-ring samples. The calcium concentration remained stable in tree-ring samples from 1740 until 1850 (Figure 12). Calcium concentrations increased beginning in 1860 and values remained elevated until 1900 when values declined by greater than one-half of the amount present a decade earlier. Calcium concentrations rose again in the following decade, 1910, and remained stable until an increase in 1960. Concentrations decreased between 1960 and 1980 with a second concentration decline during the 1990s (Figure 12).

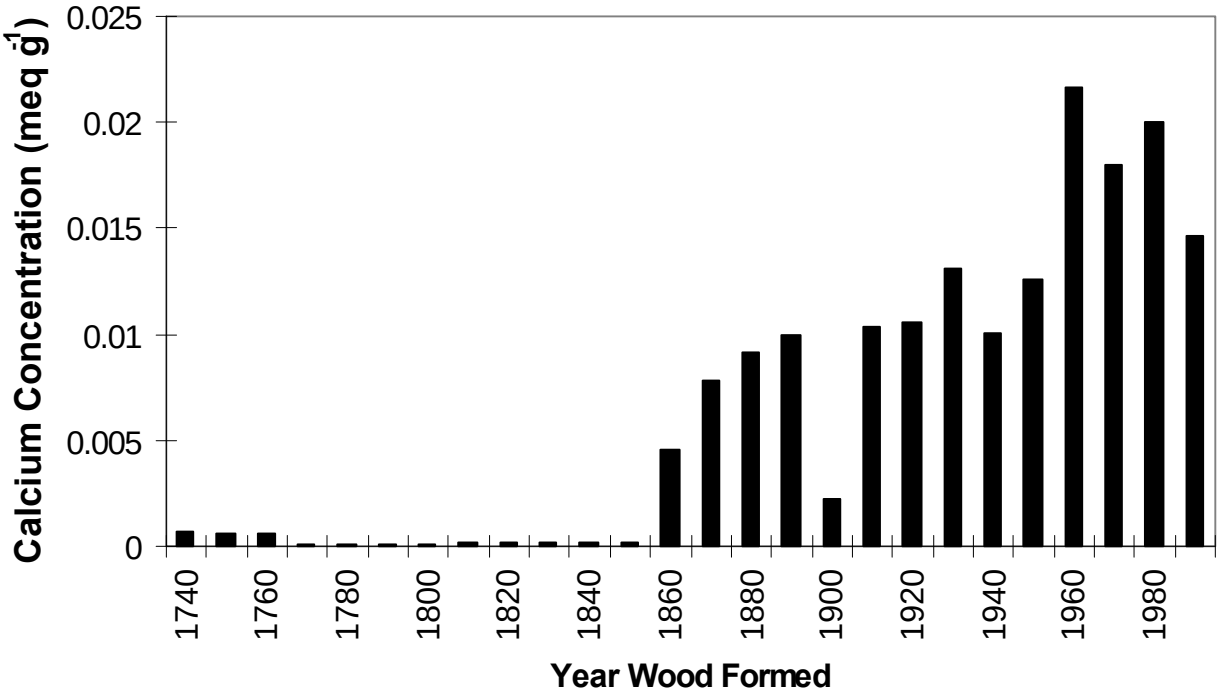

Figure 12: Calcium concentration indices through time sampled from American beech on Mount Rogers and Whitetop Mountain, Virginia.

CHAPTER 5
DISCUSSION

Dendrochronological analysis determined that the majority of American beech on Whitetop and Mount Rogers were between the ages of 40 and 110 years. Decade measurements of ring widths varied over time; however, there were no significant differences between these decadal widths. Ring-widths for samples in plots located at 1,524 meters were smaller than samples gathered from 1,371 meters, but because of different environmental conditions and topography at the 2 elevations, a specific cause could not be determined.

Most of the samples contained aluminum concentrations below the method detection limit; therefore, I could not determine if aluminum concentrations were associated with the growth of American beech trees. There are several explanations that may account for low aluminum detection. Poor recovery of aluminum using acid digestion procedures has been reported (Cronan and Grigal 1995). Based on the 85% recovery determined using the pine needle Standard Reference Material #1575, the incomplete recovery of aluminum from plant material could have resulted in low sample concentration. It is also possible that aluminum in the soil did not compete with calcium because calcium existed in higher concentrations than aluminum. Increased calcium concentration inhibits the toxicity of aluminum in roots (Joslin and Wolfe 1994). Aluminum concentrations are generally much lower in tree-rings than calcium concentrations (Watmough 1997) and this is one reason why the Al:Ca ratio in tree rings is used to normalize tree-ring chemistry.

Ring-width and cation concentration were inversely correlated. Because lead concentration and ring-width varied, additional analyses were used to evaluate the variability. As lead concentrations increased, ring-widths tended to decrease. Low lead concentration classes also corresponded to the widest ring-widths. Tree core samples taken from research plots at 1,524 meters contained higher lead concentrations than samples collected from the lower elevation plots (1,371 meters). One possible suggestion for this is the enhanced mobility of cations in soil because of the frequent exposure of higher elevation research plots to cloudwater and rain. However, to validate enhanced mobilization theories, long-term studies that include soil analyses are needed to determine changes in soil chemistry through time.

Lead toxicity varies. There are many factors that influence toxicity, including differences in tree species, charge of the cation, health of the tree, and the climate. It is also possible that toxic chemicals in the soil may reduce root growth. However, reduction of root growth may result in reduced tree growth associated with increased concentrations of metal cations (Watmough 1997). Many researchers use threshold values established for lead in soil to determine if the concentration taken up by the tree could cause a reduction in growth (e.g., Klassen et al. 2000, Smith 1981,Watmough 1997). The threshold value for soil lead phytotoxicity has been estimated at 5.79µeq g^{-1} while baseline concentrations for soil lead in the northern hardwood forest has been determined as 0.338µeq g^{-1} (Smith 1981). The maximum lead concentrations found in tree-rings on Mount Rogers and Whitetop Mountain, Virginia were between 0.25 - 0.34µeq g^{-1}; therefore, it appears that lead concentrations are at or near baseline concentrations.

Although calcium concentrations varied with aspect and decade, a statistically significant relationship between concentration and growth rate was not established. Calcium concentrations appeared to change through time, with an increase that began in 1860 and continued through 1890. Concentrations also rose again in the 1960s and 1980s. Increased calcium concentrations during these time periods were often followed by periods of decreased calcium concentrations.

Theoretical Causes for Cation Changes

While lead and calcium concentrations changed through time, my research was not designed to identify a specific cause related to this occurrence. Long-term studies would be necessary to determine if there was a specific cause for cation changes through time and the growth response in trees. Several researchers have made explanations for fluctuations in available cation concentrations found in soil and tree-rings (e.g., Smith 1981, Bondietti et al. 1990, Shortle et al. 1997, Watmough 1997). Increases in cation concentrations occurred during the 1860s, which corresponds to the beginning of the Industrial Revolution. The use of energy sources including coal and steam and the invention of the internal-combustion engine introduced large amounts of atmospheric pollutants. While there is no direct evidence that these pollutants caused changes in soil conditions that increased calcium bioavailability, it is interesting that these events correspond. Other researchers have reported sharp increases in calcium

concentrations during the 1960s and 1980s that are followed by periods of decline in concentration (e.g., Bondietti et al. 1989, Bondietti et al. 1990, Shortle et al. 1997, Watmough 1997). These researchers have speculated that this temporary increase in calcium uptake may have been caused by increased availability of essential cations in the soil (e.g., Bondietti et al. 1990, Shortle et al. 1997). Logging may also enhance the mobility of calcium in forest soils. The decrease of leaf-litter inputs, losses of dissolved organic matter, and leaching of calcium from forest soils may occur following logging (Yanai et al. 1999). Logging of Mount Rogers and Whitetop Mountain occurred beginning in the early 1900s, which corresponds to a decrease in calcium concentrations found in tree-rings.

During the 1960s and again in 1982-1988, residual ring width indices were lower than predicted values (Figure 9). Because climate variables did not adequately model growth during these time periods growth may have been influenced by nonclimatic factors. Shortle et al. (1997) stated that increased calcium concentrations in the northeastern United States, occurring in the 1960s coincided with increased levels of NO_x and SO_2. However, for a very long time deposition data were not gathered for the Mount Rogers and Whitetop Mountain research plots; therefore, reduced growth during these time periods cannot, with certainty, be attributed to increasing levels of atmospheric deposition.

Increased lead concentrations in the annual rings of trees beginning in the latter half of the 20^{th} century has been documented (e.g., Guyette et al. 1991, Kardell and Larsson 1978, Robitaille 1981, and Rolfe 1974). The majority of these studies attribute this increase to atmospheric lead deposition from automobile exhaust. Because both Mount Rogers and Whitetop Mountain are remote from large point sources of pollution, it is difficult to determine if automotive sources could influence the lead concentrations found in tree-rings. However, several researchers report that mountain summits are frequently exposed to air masses from industrial areas and this can result in high rates of hydrogen (H^+), sulfur, and heavy metal deposition (e.g., Altshuller and Linthurst 1984; and Smith 1981). Prevailing winds, precipitation, and cloudwater deposition in combination with frequent exposure to air masses from industrial areas could possibly contribute to these increased rates of deposition at higher elevations (Smith 1981). Higher average lead concentrations were found at higher elevations on Whitetop and Mount Rogers. Weathers et al. (2000) and Zechmeister (1993) also noted significant trends for high

lead concentrations at higher altitudes. In addition, it has been noted that, for mountains located in the northeastern United States, cloud deposition is significant at elevations greater than 1000m (Weathers et al. 2000).

Lead concentrations in American beech tree-ring samples from Mount Rogers and Whitetop Mountain, Virginia rose in 1920. It is interesting that this increase in lead concentration during this time period also corresponds to the introduction of leaded gasoline in 1923 (Forget and Zayed 1995). Ward et al. also noted a positive correlation between lead concentrations in trees and lead emissions from automotive sources in the 1920s (Smith 1981). Lead concentrations decreased in the following decades and gradually rose again until 1970, after which the concentrations began to decrease. The United States Congress passed legislation in the 1970s that limited use of leaded gasoline. Studies have shown decreased lead concentrations in tree-rings following the banning of leaded gasoline (e.g., Adriano 1986, Anderson et al. 2000, Johnson et al. 1995, and Watmough 1997).

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

Changes in aluminum, lead, and calcium concentrations in tree cores sampled from Mount Rogers and Whitetop Mountain in Virginia were evaluated using tree age, width per decade, concentrations per decade, and concentrations at different elevations and aspects. Concentrations of both lead and calcium varied according to aspect facing. Northwest and southwest facing aspects tended to have the highest concentrations of cations. Lead concentrations were higher in trees from research plots at 1,524 meters than those at 1,371 meters. One suggestion for this occurrence is that plots located in the high elevation ecosystems on Mount Rogers and Whitetop Mountain may have been exposed to frequent periods of cloudwater deposition and rain, increasing the occurrence of uptake. While lead concentrations appear to have increased through time, maximum lead concentrations in American beech do not appear to be above baseline concentrations or be a determinate of growth rate. Calcium concentrations found in tree-rings varied according to aspect and decade. Although calcium concentrations varied for ring-widths, the concentrations of calcium did not appear to correspond with a reduction in growth of tree-rings. Based on results from the dendrochemical analysis conducted, concentrations of aluminum and lead do not appear to exceed toxic concentrations.

In this study, aluminum concentrations were below the instrument detection limit. Therefore, in future studies the researchers should consider the use of different digestion techniques and instruments. Inductively Coupled Plasma Emission Spectrometry (ICP-ES) is a method suggested for the determination of aluminum (Watmough 1997, Tyler 1991). The use of argon plasma allows sample ashing temperatures to reach 10,000 K as compared to the nitrous oxide/acetylene flame used in flame atomic absorption at 2,900ºC (Tyler 1991). The higher temperatures used in ICP-ES improve aluminum measurement at low concentrations. The use of digestion blocks, different types of digestion vessels and materials should also be considered.

The trend of increased lead concentrations through time and the increased lead concentrations in tree-ring sampled from higher elevations, suggest further investigation of lead concentrations in vegetation and soil at Mount Rogers and Whitetop Mountain. The analysis of lead isotopes could aid in determining the origin of lead present in tree-rings. Detection of

naturally occurring lead isotopes versus those of anthropogenic origin could be investigated to determine if the lead concentrations are the result of natural lead deposits or from anthropogenic activities. Dendrochemical analysis of other cations may give researchers useful information about the uptake of additional trace metals. Examination of mercury in tree-rings in the Mount Rogers and Whitetop Mountain area could be analyzed to determine if increases in mercury concentration corresponded to periods when the Olin Corporation, in nearby Saltville, released mercury in waste disposal ponds.

Dendrochronology and dendrochemical analysis of American beech tree species appears to be a useful and innovative tool to investigate the associations of cation concentrations with growth trends in a forest ecosystem. A priori decisions concerning the species examined, the occurrence of element translocation, factors influencing growth, and area of interest aid in the use of dendrochemistry for environmental impact studies.

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APPENDIX A

Site Characteristics

Table A1.1: Site and plot characteristics of american beech dendrochronology/dendrochemistry research plots at Mount Rogers and Whitetop Mountain, Virginia.

Plot	Date	Elevation (meters)	Aspect (degrees)	Slope	Latitude	Longitude
R31	061599	1396	094	41%	363851N	813510W
R33	062299	1350	114	26%	364027N	813510W
R35	062899	1404	111	25%	363807N	813514W
R36	070699	1371	135	23%	363824N	812936W
R38	062399	1423	193	35%	363753N	813643W
R39	062499	1402	278	31%	363853N	813333W
R41	070799	1384	341	31%	364016N	813254W
R42	071599	1390	309	34%	363954N	813306W
R43	061599	1554	008	36%	363843N	813537W
R44	071699	1521	350	26%	364017N	813255W
R46	061099	1536	160	30%	363811N	813546W
R47	061899	1481	185	21%	363746N	813608W
R49	061699	1524	280	37%	363903N	813302W
R51	070999	1518	264	39%	363907N	813342W
R52	063099	1539	320	42%	363953N	813256W
R54	070199	1554	302	53%	364115N	813852W

Date= Plot establishment

APPENDIX A

Site Characteristics

Table A2.1: Tree characteristics of american beech sample trees used in dendrochronology/dendrochemistry study.

Plot	Tree Number	Age	Crown Condition	DBH (cm)
R31	6256	78	Codominant	23.5
R33	6349	100	Codominant	37.1
R33	6340	95	Codominant	24.5
R35	6507	89	Dominant	35.6
R35	6519	100	Codominant	20.4
R36	6765	75	Codominant	13.7
R36	6808	69	Codominant	24.2
R38	6363	102	Codominant	27.8
R38	6381	98	Codominant	21.4
R39	6414	127	Codominant	31.9
R39	6421	134	Codominant	37.2
R41	6850	154	Codominant	34.6
R41	6854	257	Codominant	48.0
R42	7017	222	Dominant	36.4
R42	7047	141	Dominant	28.6
R43	6099	90	Codominant	15.8
R43	6133	65	Codominant	16.0

DBH= Diameter at breast height (1.37 meters above ground)

APPENDIX A

Site Characteristics

Table A2.1 (continued): Tree characteristics of american beech sample trees used in dendrochronology/dendrochemistry study.

Plot	Tree Number	Age (years)	Crown Position	DBH (cm)
R44	7248	92	Codominant	19.4
R44	7278	80	Codominant	26.3
R46	6009	170	Dominant	37.8
R46	6055	110	Codominant	19.7
R47	6444	42	Codominant	12.6
R49	6181	62	Codominant	19.9
R49	6191	100	Dominant	21.2
R51	6995	98	Codominant	19.1
R51	7001	105	Codominant	31.8
R52	6675	56	Codominant	11.3
R52	6719	141	Dominant	27.6
R54	7061	75	Codominant	14.5
R54	7076	54	Codominant	16.3

DBH= Diameter at breast height (1.37 meters above ground)

APPENDIX B

Chemical Analysis

All methods follow Environmental Protection Agency: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846. Version 111A.

Method 7020

Aluminum (Atomic Absorption, Direct Aspiration)

1.0 Interferences

1.1 Aluminum may be as much as 15% ionized in a nitrous oxide / acetylene flame. Use of ionization suppressor (1,000 μg/ml K as KCL) as in Method 7000, Paragraph 3.1.4 will eliminate this interference.

1.2 Aluminum is a very common contaminant and great care should be taken to avoid contamination.

2.0 Apparatus and Materials

2.1 For basic apparatus see Section 4.0 of Method 7000.

2.2 Instrument parameters (general)

2.2.1 Aluminum hollow cathode lamp.

2.2.2 Wavelength: 324.7 nm

2.2.3 Fuel: Acetylene.

2.2.4 Oxidant: Nitrous Oxide

2.2.5 Type of flame: Fuel rich.

2.2.6 Background correction: Not required.

3.0 Reagents

3.1 Preparation of standards:

3.2 Stock solution: Dissolve 1.000 g of aluminum metal in dilute HCL with gentle warming. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with second standard.

3.3 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. Samples and standards should also contain 2 ml KCL / 10ml solution.

3.4 Potassium chloride solution: Dissolve 95g potassium chloride (KCL) in Type II water and dilute to 1 liter.

4.0 Method Performance

Optimum concentration range: 5-50 mg/L, with a wavelength of 309.3 nm.

Sensitivity: 1 mg/L

Detection limit: 0.1 mg/L

Method 7421

Lead (Atomic Absorption, Furnace Technique)

1.0 Interferences

1.1.1 Background correction is required

1.1.2 If poor recoveries are obtained, a matrix modifier may be necessary. 1 ml of ammonium dihydrogen phosphate may be added to 10 ml of sample.

2.0 Apparatus and Materials

2.1 Instrument Parameters (general)

2.2 Drying time and temp: 30 sec at 125°C.

2.2.1 Ashing time and temp: 30 sec at 500°C.

2.2.2 Atomizing time and temp: 10 sec at 2700°C.

2.2.3 Purge Gas: Argon

2.2.4 Wavelength 283.3 nm

2.2.5 Background correction is required

3.0 Preparation of Standards

3.1.1 Stock solution: Dissolve 1.599 g of lead nitrate, $Pb(N0_3)_2$ (analytical reagent grade), in Type II water, acidify with 10ml-redistilled $HN0_3$ and dilute to 1 ml with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

3.1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing.

4.0 Method Performance

4.1 Optimum concentration range: 5-100 µg/L

4.2 Detection limit: 1 µg/L

Method 7140

Calcium (Atomic Absorption, Direct Aspiration)

1.0 Interferences

1.1 All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc) will complex calcium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient calcium to require dilution to be in the linear range of the method.

2.0 Apparatus and Materials

2.1 Instrument Parameters

2.1.1. Calcium hallow cathode lamp

2.1.2. Wavelength: 422.7 nm.

2.1.3. Fuel: Acetylene

2.1.4. Oxidant: Nitrous oxide

2.1.5. Type of flame: stochiometric

2.1.6. Background correction: Not required

3.0 Preparation of Standards

3.1.1. Stock solution: Suspend 2.500 g of $Ca\ C0_3$ (analytical reagent grade, dried for 1 hr at 180°C) in Type I water and dissolve by adding a minimum of dilute HCL. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

3.1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing, including 1 ml of lanthanum chloride per 10 ml of sample standard.

3.1.3 Lanthanum chloride solution: Dissolve 29 g La_20_3 in 250 ml concentrated HCL. Caution- this reaction is violent!

4.0 Method Performance

4.1 Optimum concentration range: 0.2 –7 mg/L with a wavelength of 422.7 nm.

4.2 Sensitivity: 0.08 mg/L

4.3 Detection limit: 0.01 mg/L

APPENDIX C

Health and Safety

Phloroglucinol is used for staining tree cores to enhance the accurate measurement of tree-rings. One gram of phloroglucinol was dissolved in 100ml of 95% ethyl alcohol. Cores were soaked in phloroglucinol solution for one minute then removed and placed in a 50% HCL solution until they turned a red color. Health hazards for phloroglucinol include dermal, inhalation, and ingestion. Gloves, protective clothing, and eye shields were worn while handling the solution. Staining procedures occurred within a hood to prevent inhalation. No PEL or STEL have been established for phloroglucinol.

Nitrous oxide and acetylene gases were used for flame ignition. A total of 10ml nitric acid was used for the acid digestion contained within the hazard hood. Nitric acid is not combustible but will enhance the combustion of other substances. Therefore, it was kept away from flammable substances. Nitric acid hazards include: inhalation, dermal, eyes, and ingestion. To prevent exposure to such hazards nitric acid was used in an area that was ventilated well. Protective clothing, neoprene gloves, and a protection face shield were worn to prevent contact with nitric acid. The following are symptoms that occur when exposure occurs:

Symptoms associated with nitric acid exposure
Inhalation- Burning sensation, cough, trouble breathing, and unconsciousness
Dermal- Pain, yellow discoloration
Eyes- Redness, pain, severe burns
Ingestion- Abdominal pain, burning sensation, shock

Eye washing stations and showers should be used to treat dermal and eye exposure. If ingestion occurs vomiting should not be induced. Occupational Exposure Limits for nitric acid are TLV- 5.2 mg/m3, STEL -10 mg/m3, TWA-5 mg/m3 (Fisher Scientific nitric acid 16550 MSDS).

Nitrous oxide gas was used for atomic absorption in room 2 of the East Tennessee State University Environmental Health Sciences Laboratory. Extreme precautions were taken when

using any gas. Before any samples were read and the machine was turned on, gas cylinders were checked for pressure compliance and all connections fit requirements as guided by the Varian atomic absorption-operating manual. Nitrous oxide is an explosive gas; therefore, it was contained within a closed cylinder free from contact with flames. Health hazards include: inhalation, dermal, and eye pain.

Symptoms for the proceeding hazards include:

	Symptoms of gas exposure
Dermal	Frostbite (on contact with liquid)
Eyes	redness and pain.
Inhalation	Drowsiness and euphoria

Safety glasses and protective clothing were worn during sample processing to prevent exposure. Occupational Exposure Limits for nitrous oxide are the following: TLV- 90 mg/ m3, no PEL established.

Acetylene gas was mixed with air for the detection of lead on the atomic absorbance spectrometer (AA). It was important when tuning gas off at the end of the sample-processing period to turn acetylene off before air. This prevented explosion. Acetylene is an extremely flammable gas and was used with caution. The mixture of air and gas was contained within the unit. Health concerns include inhalation and dermal on contact with liquid form of the gas. Inhalation symptoms include dizziness and dullness. Frostbite can occur is liquid form is encountered; however, with sample processing on the AA this did not occur. The auto-ignition temperature for acetylene gas is 299 degrees Celsius. TLV and PEL are not established.

APPENDIX D

Table D4.1: Actual and predicted tree-ring widths for American beech generated from the final regression model.

Year	May Precipitation	Predicted Width	Actual Width	Residuals
1945	.	.	1.079	
1946	7.25	1.09	1.102	0.010791
1947	.	.	0.959	.
1948	9.2	1.15	1.104	-0.04571
1949	5.09	1.03	1.071	0.044591
1950	5.31	1.03	1.081	0.047991
1951	2.88	0.96	1.022	0.061891
1952	2.89	0.96	1.098	0.137591
1953	5.7	1.04	1.06	0.015291
1954	4.47	1.01	1.079	0.071191
1955	2.12	0.94	1.039	0.101691
1956	3.88	0.99	1.06	0.069891
1957	6.28	1.06	0.959	-0.10311
1958	5.27	1.03	0.989	-0.04281
1959	3.69	0.98	0.991	0.006591
1960	3.23	0.97	0.892	-0.07861
1961	4.43	1.01	0.939	-0.06761
1962	3.6	0.98	0.951	-0.03071
1963	3.66	0.98	0.876	-0.10751
1964	2.49	0.95	0.916	-0.03241
1965	3.47	0.98	0.900	-0.07781
1966	2.48	0.95	0.925	-0.02311
1967	5.23	1.03	0.932	-0.09861
1968	5.6	1.04	0.974	-0.06771
1969	2.15	0.94	0.837	-0.10121

Year	May Precipitation	Predicted Width	Actual Width	Residuals
1970	1.06	0.91	0.908	0.002491
1971	6.67	1.07	1.079	0.005191
1972	5.46	1.04	1.099	0.061491
1973	6.84	1.08	1.216	0.137091
1974	5.8	1.05	0.979	-0.06871
1975	4.93	1.02	0.925	-0.09661
1976	2.79	0.96	0.907	-0.05041
1977	1.7	0.92	0.894	-0.03071
1978	4.36	1.00	0.954	-0.05051
1979	4.54	1.01	1.008	-0.00191
1980	2.89	0.96	0.856	-0.10441
1981	5.65	1.04	1.000	-0.04321
1982	5.37	1.03	1.003	-0.03181
1983	3.93	0.99	0.933	-0.05861
1984	5.14	1.03	0.796	-0.23191
1985	3.99	0.99	0.81	-0.18341
1986	4.66	1.01	0.877	-0.13651
1987	2.87	0.96	1.028	0.068191
1988	2.89	0.96	1.021	0.060591
1989	4.82	1.02	1.022	0.003691
1990	4.66	1.01	1.147	0.133491
1991	4.37	1.00	1.111	0.106191
1992	4.16	1.00	0.953	-0.04551
1993	2.83	0.96	0.972	0.013391
1994	1.99	0.93	0.902	-0.03141
1995	3.62	0.98	1.013	0.030691
1996	5.66	1.04	0.985	-0.05851
1997	2.08	0.94	1.059	0.122891
1998	7.35	1.09	1.059	-0.03521
1999	3.63	0.98	0.79	-0.19261

APPENDIX D

Table D4.2: Historical precipitation data from Chilhowie/Alexandria weather stations (inches) and Arstan ring-width indices.

Station	year	Jan	Feb	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Nov	Dec	Width (mm)
ALEXANDRIA	1945	.	.	.	.	.	.	.	.	.	0.67	3.54	.	1.079
ALEXANDRIA	1946	1.6	2.3	1.8	2.1	7.25	2.37	3.92	5.67	2.29	.	.	.	1.102
ALEXANDRIA	1947	.	.	.	.	.	.	.	.	.	2.79	4.17	1.7	0.959
ALEXANDRIA	1948	5.4	2.2	3.49	3.74	9.2	4.68	3.95	8.31	3.2	2.79	5.75	4.57	1.104
ALEXANDRIA	1949	4.67	.	3	2.2	5.09	2.56	4.06	4.25	3.59	3.14	0.86	1.96	1.071
ALEXANDRIA	1950	1.63	2.25	3.89	1.58	5.31	3.65	4.42	4.2	5.05	2.65	2.33	3.02	1.081
ALEXANDRIA	1951	2.05	2.58	2.42	3.52	2.88	5.52	4.13	1.54	1.42	1.44	5.08	5.21	1.022
CHILHOWIE	1953	2.92	3.85	4.43	2.61	5.7	4.55	2.45	2.86	2.63	1.82	1.03	4.22	1.06
CHILHOWIE	1954	6.28	0.66	3.92	2.81	4.47	0.56	5.7	4.35	0.78	2	2.36	3.35	1.079
CHILHOWIE	1956	1.69	5.81	5.1	4.06	3.88	1	5.26	2.8	3.82	1.28	2.63	3.6	1.06
CHILHOWIE	1957	8.93	6.6	2.81	4.38	6.28	3.07	1.9	2.59	6.14	1.79	4.89	4.27	0.959
CHILHOWIE	1958	2.06	3.38	3.11	4.13	5.27	2.85	7.61	5.23	0.55	1.27	3.12	2.36	0.989
CHILHOWIE	1959	2.65	2.12	3.19	5.55	3.69	3.73	3.87	3.18	3.67	6.27	3.46	2.77	0.991
CHILHOWIE	1960	2.8	3.79	4.17	1.74	3.23	3.03	4.05	5.12	1.46	3.1	1.72	1.43	0.892
CHILHOWIE	1961	2.12	5.33	3.66	3.34	4.43	5.1	4.44	4.11	2.99	3.55	2.77	6.83	0.939
CHILHOWIE	1962	4.98	5.83	3.51	2.36	3.6	5.56	5.57	3.27	4.1	1.92	2.96	4.94	0.951
CHILHOWIE	1964	3.68	3.94	4.07	3.28	2.49	1.93	4.83	2.74	2.97	5.49	1.98	2.68	0.916
CHILHOWIE	1965	3.46	2.33	5.18	3.4	3.47	3.81	6.28	4.06	1.46	2.18	1.6	0.34	0.9
CHILHOWIE	1966	3.24	3.22	2.23	5.2	2.48	1.7	5.6	4.15	6.28	3.75	3.33	3.62	0.925
CHILHOWIE	1967	1.89	3.67	3.01	5.25	5.23	3.56	4.44	3.35	3.11	2.63	2.41	4.83	0.932
CHILHOWIE	1968	4.4	0.45	3.57	4.82	5.6	1.51	3.28	4.59	1.42	4.54	2.13	2.49	0.974
CHILHOWIE	1970	3.46	2.66	2.48	6.67	1.06	1.73	3.77	4.33	2.9	2.6	3.12	3.51	0.908
CHILHOWIE	1971	4.22	4.36	2.81	3.25	6.67	5.12	6.27	5	2.73	4.74	2.42	1.47	1.079
CHILHOWIE	1972	6.28	4.29	1.82	4.18	5.46	5.68	5.16	4.98	7.29	3.95	3.91	6.35	1.099

Table D4.3: Decade class values assigned used in analysis of variance between ring width and decade class.

Decade	Decade Class Assigned
1990-1999	1
1980-1989	2
1970-1979	3
1960-1969	4
1950-1959	5
1940-1949	6
1930-1939	7
1920-1929	8
1910-1919	9
1900-1909	10
1890-1899	11
1880-1889	12
1870-1879	13
1860-1869	14
1850-1859	15
1840-1849	16
1830-1839	17
1820-1829	18
1810-1819	19
1800-1809	20
1790-1799	21
1780-1789	22
1770-1779	23
1760-1769	24
1750-1759	25
1740-1749	26

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